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I. *The Analysis of Compound Wave Forms.* *By* J. S. THOMPSON, *B.A.* (Communication from the Staff of the Research Laboratories of The General Electric Company, Limited, Wembley, England *.)

[Plates I. & II.]

SUMMARY.

THE analysis of a wave form compounded of a pair of sine waves, although presenting no theoretical difficulty, is often laborious in practice. The following paper classifies the forms which may arise, and provides a convenient method for performing the analysis.

ANYONE who uses an oscillograph, or any other form of vibration recorder, will frequently be confronted by the problem of the analysis of a composite wave produced by the superposition of two or more true sine waves. There is no theoretical difficulty about the complete analysis of such a record, but the practical difficulties are considerable when more than two frequencies are present. When there are only two frequencies, however, the analysis is relatively simple, though puzzling at first sight.

The problem was encountered by the writer in connexion with vibrations of turbine disks. When a vibration in a rotating turbine disk consists of a forward travelling wave

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and a backward travelling wave, the record obtained by a stationary "pick up" consists of two superimposed sine waves of different frequencies. For the analysis of these records some rules were formulated, which are here described for the benefit of others who may encounter the same problem.

Section I. illustrates different types of composite records which may be produced, and a description is given of how the oscillograms shown in figs. 1–8 (Pls. I. & II.) were obtained. Section II. establishes a few mathematical relations, which are needed for Section III., in which the methods of analysis are described in detail.

I. Illustrations of Typical Records.

Figs. 1–8 (Pls. I. & II.) illustrate types of records obtained by the combination of two pure sine waves. In each case the upper and lower records represent the component waves, and the centre record the composite wave obtained by the addition of the two.

The composite waves may conveniently be classified into three groups as follows:

Class I. Waves with pronouced beats, as shown in figs. 1–3 (Pl. I.).

Class II. Waves with less pronounced, but quite definite beats, as in figs. 4 and 5 (Pls. I. & II.).

Class III. Waves without beats, as in figs. 6–8 (Pl. II.).

It will be noticed that in records of Class II. or III. one frequency can be picked out at sight, but in Class I. records this is not so easy. In fig. 3 (Pl. I.), for instance, the wave completely loses its form at the places of smallest amplitude, so that the peaks cannot be counted directly.

The frequencies and amplitudes of the component waves in figs. 1–8 (Pls. I. & II.) are given in the table.

A description of how the oscillograph records were obtained may be of interest, for some difficulty was found in getting a suitable variable frequency supply of pure enough wave form. Eventually an apparatus was used which had been developed for recording turbine disk vibrations. This consisted of an insulated metal plate fixed close to the rim of the disk so that the vibration of the disk caused a variation of capacity between the plate and disk, and this variation, by means of a suitable amplifier, was recorded on an oscillograph. For the purposes of this test a small rigid

disk was used, mounted not quite perpendicular to its shaft, thus producing a true sine wave of a frequency equal to the speed of rotation of the disk. This gave a variable frequency wave, and for the other wave the 50-cycle mains were used.

II. Theoretical Treatment.

Let $$y = a_1 \cos(\omega_1 t + \epsilon_1), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$y = a_2 \cos(\omega_2 t + \epsilon_2), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

be two component waves, a_1 being the larger of the amplitudes. The frequencies $\frac{\omega_1}{2\pi}$ and $\frac{\omega_2}{2\pi}$ of the two waves will be denoted by f_1 and f_2 respectively.

Table.

Figure.	a_1.	f_1.	a_2.	f_2.
1	1·45	54·2	1·05	50·0
2	1·35	46·4	1·05	50·0
3	1·2	50·0	1·1	46·2
4	2·1	50·0	·5	54·2
5	2·1	50·0	·4	44·8
6	1·1	85·2	1·1	50·0
7	2·05	50·0	·4	85·5
8	1·45	50·0	·75	89·2

Note.—The above amplitudes are in inches (on the original records), and the frequencies in cycles/second.

The equation of the composite wave produced by the superposition of (1) and (2) is :

$$y = a_1 \cos(\omega_1 t + \epsilon_1) + a_2 \cos(\omega_2 t + \epsilon_2). \quad . \quad . \quad (3)$$

Case I.—ω_1 nearly equal to ω_2.

This case, as will be seen later, covers Classes I. and II. of the preceding section.

Equation (3) may be rewritten :

$$y = (a_1 + a_2)\left[\cos\left\{\tfrac{1}{2}(\omega_1 + \omega_2)t + \tfrac{1}{2}(\epsilon_1 + \epsilon_2)\right\} \times \cos\left\{\tfrac{1}{2}(\omega_1 - \omega_2)t + \tfrac{1}{2}(\epsilon_1 - \epsilon_2)\right\}\right]$$

$$-(a_1 - a_2)\left[\sin\left\{\tfrac{1}{2}(\omega_1 + \omega_2)t + \tfrac{1}{2}(\epsilon_1 + \epsilon_2)\right\} \times \sin\left\{\tfrac{1}{2}(\omega_1 - \omega_2)t + \tfrac{1}{2}(\epsilon_1 - \epsilon_2)\right\}\right].$$

Now if ω_1 is nearly equal to ω_2, then $(\omega_1-\omega_2)t$ is changing slowly compared with $(\omega_1+\omega_2)t$. Thus we may write:

$$y=\mathrm{A}\cos\{\tfrac{1}{2}(\omega_1+\omega_2)t+\theta+\tfrac{1}{2}(\epsilon_1+\epsilon_2)\}, \quad . \quad . \quad (4)$$

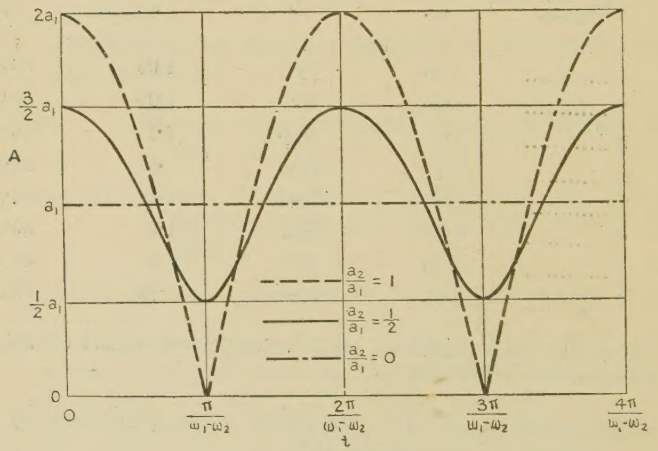
where

$$\mathrm{A}^2=(a_1+a_2)^2\cos^2\{\tfrac{1}{2}(\omega_1-\omega_2)t+\tfrac{1}{2}(\epsilon_1-\epsilon_2)\}$$
$$+(a_1-a_2)^2\sin^2\{\tfrac{1}{2}(\omega_1-\omega_2)t+\tfrac{1}{2}(\epsilon_1-\epsilon_2)\}$$
$$=a_1^2+a_2^2+2a_1a_2\cos\{(\omega_1-\omega_2)t+(\epsilon_1-\epsilon_2)\}$$

and

$$\tan\theta=\frac{a_1-a_2}{a_1+a_2}\tan\{\tfrac{1}{2}(\omega_1-\omega_2)t+\tfrac{1}{2}(\epsilon_1-\epsilon_2)\}.$$

Fig. 9.



Equation (4) may be taken as representing (roughly) a cosine wave of frequency $\frac{1}{4\pi}(\omega_1+\omega_2)=\frac{1}{2}(f_1+f_2)$, whose amplitude A and phase angle θ are each slowly changing.

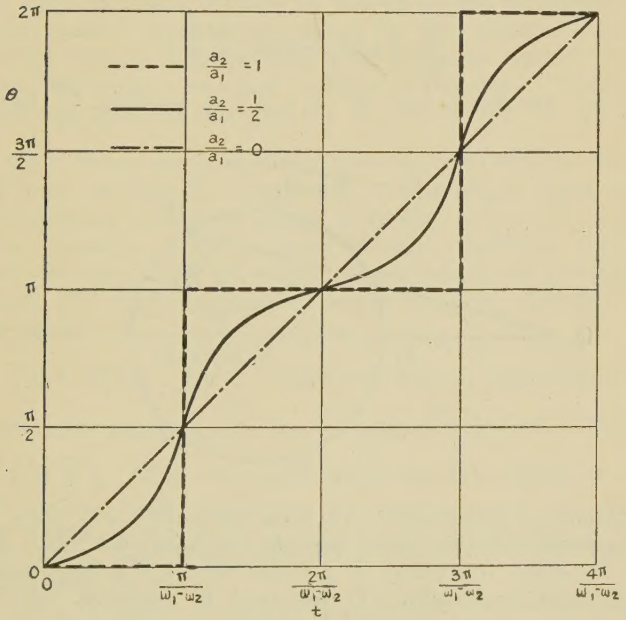
The fluctuation of the amplitude is shown in fig. 9, where A, or $\sqrt{a_1^2+a_2^2+2a_1a_2\cos\{(\omega_1-\omega_2)t+(\epsilon_1-\epsilon_2)\}}$ is plotted against t for three values of $\frac{a_2}{a_1}$, viz., 0, $\frac{1}{2}$, and 1, a suitable time origin being chosen to make $\epsilon_1-\epsilon_2=0$. The curves illustrate how the range of fluctuation alters as the ratio

$\frac{a_2}{a_1}$ is changed; the frequency of fluctuation is in every case $\frac{\omega_1-\omega_2}{2\pi}$, which is equal to the "beat frequency" (f_1-f_2).

The manner in which θ varies is shown on fig. 10, where

$$\theta, \quad \text{or} \quad \tan^{-1}\left[\frac{a_1-a_2}{a_1+a_2}\tan\{\tfrac{1}{2}(\omega_1-\omega_2)t+\tfrac{1}{2}(\epsilon_1-\epsilon_2)\}\right],$$

Fig. 10.



is plotted against t for the same three values of the ratio $\frac{a_2}{a_1}$. It will be seen that if $\frac{a_2}{a_1}=1$, θ increases in discontinuous jumps of π at time intervals of $\frac{2\pi}{\omega_1-\omega_2}$; if $\frac{a_2}{a_1}=0$, θ increases at a uniform rate, and is everywhere equal to $\frac{1}{2}(\omega_1-\omega_2)t$; while if $\frac{a_2}{a_1}$ has a value between 0 and 1, θ increases continuously, but not uniformly, as shown by the wavy line on fig. 10.

A comparison between figs. 9 and 10 shows that if $\frac{a_2}{a_1}$ is nearly equal to unity, the phase angle changes by π where

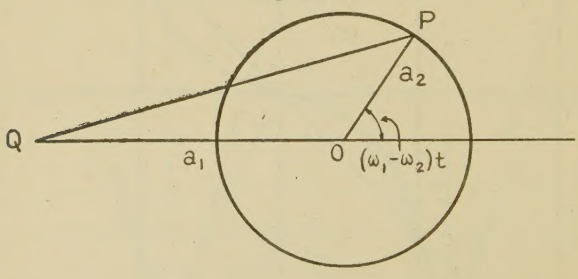
the amplitude is a minimum in each "beat," but is sensibly constant elsewhere. Thus equation (4) shows that the wave has a practically constant frequency $\frac{1}{2}(f_1+f_2)$, but undergoes a reversal of phase at places where its amplitude is least. This suggests a method of analysing such a record, which is described in the next section.

If $\frac{a_2}{a_1}$ lies between 0 and 1, the effect of the variation of θ is to produce an apparent fluctuation of frequency of the wave given by equation (4). This frequency is

$$\frac{1}{2\pi}\left\{\tfrac{1}{2}(\omega_1+\omega_2)+\frac{d\theta}{dt}\right\},$$

and fig. 10 shows that if $(\omega_1-\omega_2)$ is positive, $\frac{d\theta}{dt}$ has its

Fig. 11.



maximum value where $(\omega_1-\omega_2)t=\pi$, 3π, 5π, etc., and its minimum value where $(\omega_1-\omega_2)t=0$, 2π, 4π, etc. Thus the apparent frequency is greatest where the amplitude is least, and conversely. If $(\omega_1-\omega_2)$ is negative, however, θ is always decreasing, and the above argument shows that the apparent frequency is least where the amplitude is least, and conversely. These points also are useful for measuring records.

The variation of A and θ may conveniently be illustrated by the diagram shown in fig. 11. OP is a vector, length a_2, rotating with angular velocity $(\omega_1-\omega_2)t$. Q is a fixed point such that $OQ=a_1$ and QOP is a straight line at time $t=0$. Then $A=PQ$, and $\theta=\frac{1}{2}(\angle P-\angle Q)$. The limiting case when $\frac{a_2}{a_1}=0$ may be illustrated by making $OQ=\infty$, and he case $\frac{a_2}{a_1}=1$, by making Q lie on the circle. In each case the conclusions obtained above may readily be verified.

Case 2.—ω_1 and ω_2 not nearly equal.

When the component frequencies are not nearly equal, each problem has to be treated separately, and classification or analysis of the general case is not practicable.

The following general notes are useful for determining amplitudes :—

(i.) The maximum possible excursion, from the zero line, of the composite wave is $\pm(a_1+a_2)$. It is not strictly accurate to assume that the wave ever reaches this value on any particular section of record to be analysed, but in most cases it comes near enough for the extreme excursions of the wave to give $(a_1 \mp a_2)$ with sufficient accuracy, unless one frequency is an exact multiple of the other. This special case is treated in note (v.).

(ii.) When one component wave is small and has the effect of only varying the amplitude of the larger wave without introducing additional peaks, as in figs. 4, 5, 7 (Pls. I. & II.), the minimum possible value of this amplitude is (a_1-a_2) and the maximum (a_1+a_2). These values are best obtained from the bounding curve, which may be sketched in as in fig. 12.

(iii.) When $\frac{f_1}{f_2}=\frac{n_1}{n_2}$, where n_1 and n_2 are integers, the composite wave repeats itself identically at time intervals of $\frac{n_1}{f_1}\left(=\frac{n_2}{f_2}\right)$. This is a useful point, for low values of n_1 and n_2 usually exist which satisfy this condition approximately, producing an obvious similarity between two points of the composite wave.

(iv.) If values of n_1 and n_2 be chosen so that one is odd and the other even, and a point be found where the amplitude is (a_1+a_2), then since the component waves reach their maximum together at this peak, they will also reach their maximum together at another peak after n_1 cycles of f_1 and n_2 cycles of f_2. Therefore, at a point midway between these peaks, one wave will be a maximum and the other a minimum, giving a distance from the zero line of (a_1-a_2) if n_1 is even and n_2 odd, or (a_2-a_1) if n_2 is even and n_1 odd.

(v.) The foregoing methods for determining the amplitudes of the component waves cannot be applied when one frequency is an exact multiple of the other, unless the two waves reach their maximum values at the same time, enabling (a_1+a_2) to be measured. The following method may be used instead.

Let

$$y = a_1 \cos(\omega t + \epsilon_1) + a_2 \cos(n\omega t + \epsilon_2)$$

be the composite wave. The positions of the peaks and troughs of the higher frequency wave can be determined fairly accurately, as described in the next section. At the peaks of the high frequency wave,

$$\cos(n\omega t + \epsilon_2) = +1,$$

$$\therefore \quad \omega t = \frac{1}{n}(2r\pi - \epsilon_2);$$

$$\therefore \quad y_{2r} = a_1 \cos\left(\epsilon_1 - \frac{\epsilon_2}{n} + \frac{2r\pi}{n}\right) + a_2,$$

and at the troughs

$$\cos(n\omega t + \epsilon_2) = -1;$$

$$\therefore \quad \omega t = \frac{1}{n}\{(2r-1)\pi - \epsilon_2\};$$

$$\therefore \quad y_{2r-1} = a_1 \cos\left\{\epsilon_1 - \frac{\epsilon_2}{n} + \frac{(2r-1)\pi}{n}\right\} - a_2.$$

Summing these ordinates over one cycle of the low frequency wave, we obtain :

$$\sum_{r=1}^{r=n} y_{2r} = a_1 \sum_{r=1}^{r=n} \cos\left(\epsilon_1 - \frac{\epsilon_2}{n} + \frac{2r\pi}{n}\right) + na_2 = na_2 \quad . \quad (5)$$

and

$$\sum_{r=1}^{r=n} y_{2r-1} = -na_2, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and summing the squares of the ordinates

$$\sum_{r=1}^{r=n} y_{2r}^2 + \sum_{r=1}^{r=n} y_{2r-1}^2 = a_1^2 \sum_{r=1}^{r=2n} \cos^2\left(\epsilon_1 - \frac{\epsilon_2}{n} + \frac{r\pi}{n}\right) + 2na_2^2,$$

$$+ 2a_1a_2 \sum_{r=1}^{r=n} \cos\left(\epsilon_1 - \frac{\epsilon_2}{n} + \frac{2r\pi}{n}\right)$$

$$- 2a_1a_2 \sum_{r=1}^{r=n} \cos\left\{\epsilon_1 - \frac{\epsilon_2}{n} + \frac{(2r-1)\pi}{n}\right\}$$

$$= na_1^2 + 2na_2^2. \quad . \quad (7)$$

These relations enable a_1 and a_2 to be obtained from the ordinates $y_1, y_2, \ldots y_{2n}$. If the equations (5) and (6) do not agree, it is an indication that another frequency is present,

but if the difference is small, the average result may be used to give a good approximate value of a_2.

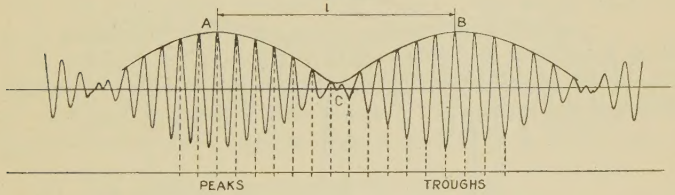
Further details which are occasionally useful will be found in the next section, describing the practical analysis of records.

III. Practical Analysis of Records.

In an oscillograph or similar recording instrument the record is made on a moving strip of paper. Some form of timing device is used to record the paper speed v, and the frequency f of any wave can be measured by counting the number of cycles n in a length l on the paper. Then $f = \frac{nv}{l}$.

In the following descriptions it is assumed that the paper speed is known, and it is required to obtain the amplitudes

Fig. 12.



a_1 and a_2, and the frequencies f_1 and f_2 of the composite waves shown in figs. 1–8 (Pls. I. & II.).

It is convenient to classify records as described in Section I., and a detailed description will be given of methods applicable in each case.

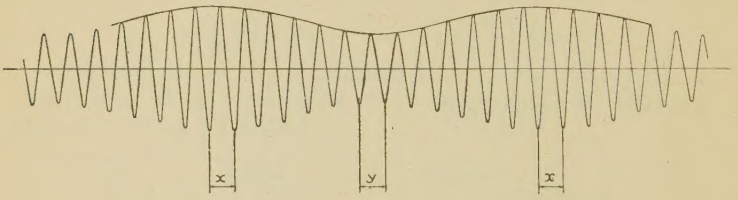
Class I.—Pronounced Beats.

The procedure in this case is to measure the average frequency $\frac{1}{2}(f_1+f_2)$ and the beat frequency (f_1-f_2). The method is illustrated in fig. 12, which is traced from fig. 3 (Pl. I.). The length l may be measured between any two peaks of large amplitude, such as A and B on fig. 12, and the number of cycles n for the average frequency is obtained by marking the peaks of one "beat," the troughs of the next, the peaks of the next, and so on. (This is necessary because of the reversal of phase explained in Section II.) These cycles are marked in fig. 12, and it will be seen that they occur at equal intervals, so that if any difficulty is experienced in locating the peaks at places of minimum amplitude, the

points may be easily interpolated. The number of cycles between A and B is $12\frac{1}{2}$. (A half cycle will always be introduced when the measurement is made over an odd number of beats.) The beat frequency may be measured by sketching in the bounding curve of the wave as shown, and measuring between the peaks of this curve. In this instance the average frequency is 48·1 cycles/second, and the beat frequency 3·8 cycles/second, giving component frequencies 50·0 and 46·2 cycles/second. It will be found that the beat frequency cannot be measured very accurately, but as it is small it does not affect the accuracy with which f_1 and f_2 can be measured.

In order to obtain the amplitudes, the zero line must first be drawn in midway between the points of maximum excursion on either side. Since the ratio of the frequencies is $\frac{50}{46{\cdot}2}=\frac{13}{12}$, we may take $n_1=13$, $n_2=12$, as described in

Fig. 13.



note (iv.) of the previous section, and taking A as one maximum peak and B as the next, the point C may be obtained midway between. Since n_1 is odd, this point gives (a_2-a_1) which, as C is below the zero line, is negative. Thus the frequency 50, which has been called f_1, corresponds to the larger of the two amplitudes.

In this particular record the two amplitudes are so nearly equal that it is difficult to determine (a_2-a_1) accurately. Separate measurements may be made for each beat, however, and an average value obtained. It is to be noted that any slight departure from a true sine shape in either of the component waves will be exaggerated at places of small amplitude, where the fundamentals practically cancel each other, but any harmonics do not.

Class II.—Less Pronounced Beats.

When the beats are less pronounced, as in fig. 13, traced from fig. 4 (Pl. I.), the method described for Class I. will

be found inapplicable, but one of the component frequencies may be easily measured. Since the phase angle of the wave is changing, it is best to measure between two peaks of maximum amplitude, where the phase is changing least rapidly. The beat frequency $f_1 - f_2$ may be obtained from the peaks of the bounding curve. It remains to find whether the predominating frequency is the higher or the lower of the two component frequencies. This is done by comparing the spacing of the peaks at the places of greatest and least amplitudes. If the large peaks are more widely spaced than the small ones, the predominant frequency is the higher of the two ; if the smaller peaks are more widely spaced, the predominant frequency is lower. In fig. 13 y is larger than x, so that the predominant frequency is lower, and the beat frequency has to be added to obtain the other frequency. The amplitudes of the component waves may be obtained from the distance of the bounding curve from the zero line, the maximum distance being $(a_1 + a_2)$ and the minimum distance $(a_1 - a_2)$. The larger amplitude a_1 is associated with the predominant frequency.

A record of this type may easily be confused with a modulated sine wave, which is composed of *three* frequencies, a "carrier" and two "side bands." The chief distinguishing features of a wave such as figs. 4 or 5 (Pls. I. & II.) are :

(*a*) The unequal spacing of the peaks.

(*b*) The bounding curve is not truly sinusoidal, but has a sharper curvature when close to the zero line than when far from it (see fig. 9).

Class III.—No Beats.

The variety of records in this class is so great that it is not possible to formulate any hard and fast rules. The analysis of four characteristic records will be described, and this will serve to illustrate the most useful methods to employ.

When one frequency is much larger than the other, say three times or more, the analysis presents no difficulty, and need not be discussed in detail. When the low-frequency wave is smaller, its frequency and amplitude may be obtained from the bounding curve of the high-frequency wave; and when the high-frequency wave is smaller, it appears as a ripple on the low-frequency wave, and can easily be separated.

In fig. 14, which is traced from fig. 6 (Pl. II.), the higher frequency is readily picked out. The presence of

the lower frequency may be seen, but its conspicuous peaks occur irregularly, and it is difficult to count them. The conspicuous peaks and troughs may be marked off, however, as shown in fig. 13, and sufficient points are thus obtained to count the number of cycles, as shown by the lower line of marks. As usual, it is best to measure l between two peaks of maximum amplitude, such as A and B.

The amplitudes may be determined by the method described above in note (iv.) of Section II. A and B are two maximum peaks, giving (a_1+a_2), and between A and B there are 15 cycles of the lower frequency and 26 of the higher. The peak C, midway between, gives (a_1-a_2), which in this case is zero.

Fig. 14.

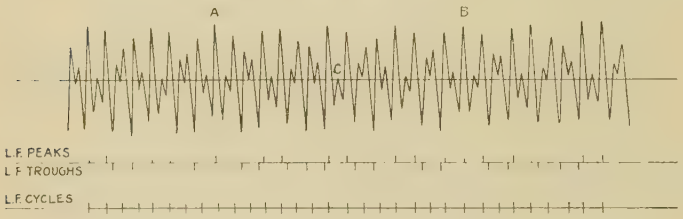


Fig. 15.

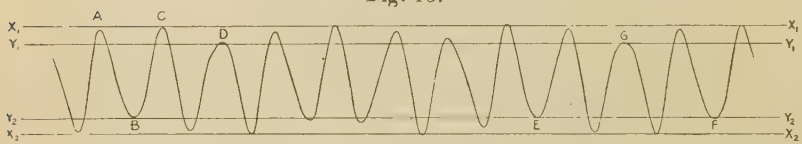


Fig. 15, which is traced from fig. 7 (Pl. II.), is a record in which only one frequency is conspicuous. The values of a_1 and a_2 may, however, easily be determined by drawing lines, as shown, through the minimum and maximum peaks on each side of the zero line. The distances between the pairs of lines X_1X_1, X_2X_2, and Y_1Y_1, Y_2Y_2, are $2(a_1+a_2)$ and $2(a_1-a_2)$ respectively.

The larger amplitude is associated with the conspicuous frequency, which is found to be 50 cycles/second. If the second frequency were about 14 cycles/second, this would account for the general form of the composite wave, but on closer inspection it will be seen that some of the peaks show considerable distortion, which could not be caused by a small amplitude wave of this frequency. If, then, the record is known to consist of two pure sine waves, the

following method may be used to determine the second frequency. Consider the three points A, B, C. The point B is one of the least troughs of the record; accordingly at this point the component wave No. 1 (the larger of the two) is a minimum, and No. 2 wave a maximum. A and C are points of nearly maximum peaks, where the two waves must reach a maximum about the same time. The smoothness of the curve between A and B, and between B and C, shows that No. 2 wave has no other maximum values between these points, so between A and C there are about two cycles of f_2 and one of f_1. Thus as a first approximation $f_2 = 2f_1$.

Next it can be found by measurement that the distance between the peaks A and C is rather greater than the average distance between the peaks along the record, so that the length of two cycles of f_2 is rather more than that of one cycle of f_1. Thus as a second approximation f_2 is slightly less than $2f_1$. Next consider peak D. It may be seen that just as B indicates the coincidence of a peak of No. 2 wave with a trough of No. 1, so D indicates that a trough of No. 2 nearly coincides with a peak of No. 1. From B to D is $1\frac{1}{2}$ cycles of No. 1, so it must be about $1\frac{1}{2}$, $2\frac{1}{2}$, or $3\frac{1}{2}$ cycles of No. 2. The second approximation shows that it can only be $2\frac{1}{2}$, so as a third approximation we have

$$f_2 = \frac{2\frac{1}{2}}{1\frac{1}{2}} f_1 = \frac{5}{3} \times 50 = 83 \text{ cycles/second, about.}$$

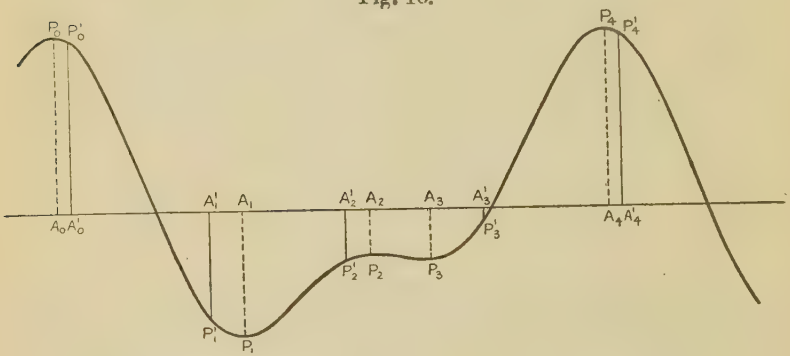
Finally, it will be seen that peaks B and E correspond nearly identically, as regards the shape of the curve in the neighbourhood, so that, since between B and E there are seven cycles of No. 1, there must be an integral number of cycles of No. 2, say n. Thus $f_2 = \frac{n}{7} \times 50$, and as 83 is an approximate value, n must be 12, giving $f_2 = 85{\cdot}6$. It is best to check this by finding other pairs of points and taking the mean of the frequencies obtained. Thus points B and F give 17 and 10, making $f_2 = 85$; points B and G give $14\frac{1}{2}$ and $8\frac{1}{2}$, making $f_2 = 85{\cdot}3$. Thus $85{\cdot}3$ may be taken as the average value, and probably most accurate.

Fig. 8 (Pl. II.) represents a record where each frequency can be measured directly without difficulty, for each peak of the higher frequency wave shows up either as a peak or as a definite "kink" in the composite wave. In counting these high-frequency cycles it is best to mark off each peak, as was done for the low-frequency wave in fig. 14. This avoids the danger of missing a peak, for the peaks will occur at equal

intervals, and it will be easy to see whether a doubtful "kink" should be counted. The amplitudes can be determined as described above (in note iv.): a suitable value of n_1/n_2 is 9/16, which is nearly equal to the frequency ratio 50/89·2.

Fig. 16 illustrates the method of measuring the amplitudes when one frequency is an exact multiple of the other. In this case the ratio of the frequencies is 2, and the frequencies may be measured without difficulty. The peaks and troughs of the higher frequency wave are located as follows. As a first approximation the peaks and troughs, P_0, P_1, P_2, P_3, P_4, of the composite wave are taken, and perpendiculars from these to the zero line give the points A_0, A_1, A_2, A_3, A_4. These points are not equally spaced, but the length A_0A_4 divided by four gives the correct

Fig. 16.



spacing for the peaks of the higher frequency wave, and their positions, A_0', A_1', A_2', A_3', A_4', are obtained by making the algebraic sum of the distances A_0A_0', A_1A_1', A_2A_2', A_3A_3', equal to zero. In this case the distances from A_0 of the points A_1, A_2, A_3, A_4 are 3·0″, 5·1″, 6·2″, and 9·0″ respectively, and the appropriate distances from A_0 of the points A_0', A_1', A_2', A_3', A_4' are found to be 0·2″, 2·45″, 4·7″, 6·95″, and 9·2″ respectively. Then the points A_0', A_2', A_4 represent the places where the higher frequency wave is a maximum, and the points A_1', A_3' where it is a minimum. The ordinates at these points are as follows:

$$A_0'P_0' = \ 2{\cdot}85'', \qquad A_1'P_1' = -1{\cdot}75'',$$
$$A_2'P_2' = -0{\cdot}85'', \qquad A_3'P_3' = -0{\cdot}25''.$$

Then if a_1 be the amplitude of the low-frequency wave, and a_2 that of the high-frequency wave,

$$2a_2 = 2{\cdot}85 - 0{\cdot}85 = -(-1{\cdot}75 - 0{\cdot}25)$$
$$\therefore \quad a_2 = 1{\cdot}0''$$

and

$$2a_1^2 + 4a_2^2 = (2{\cdot}85)^2 + (0{\cdot}85)^2 + (1{\cdot}75)^2 + (0{\cdot}25)^2$$
$$= 11{\cdot}97$$
$$\therefore \quad a_1 = 2{\cdot}0''.$$

The general formulæ for other frequency ratios are given in Sect. II. (equations (5), (6), (7)), but, as explained above, it is not necessary to apply this method when the ratio is high and the bounding curves can be drawn in.

General Remarks.

The various methods of measurement outlined above will suffice for most practical cases of analysis of composite waves of two frequencies. Care must be exercised when it is suspected that other frequencies may be present, especially in the case of the modulated wave mentioned in the analysis of fig. 4 (Pl. I.). The method of successive approximations used for fig. 7 (Pl. II.) must also be employed with care, but the method for fig. 3 (Pl. I.) may be used quite freely whenever the peaks of one beat and the troughs of the next form an equally spaced series, as in fig. 12.

Frequencies may generally be measured much more accurately than amplitudes, due to the longer lengths to be measured, but when both frequencies have been determined the method of amplitude measurement decribed in Section II., note (iv.) is nearly always applicable. The method of note (ii.) is useful to determine the larger amplitude in case there is a doubt about the frequency of the smaller wave, as would happen in fig. 4 or fig. 7 if other frequencies were present.

II. *The Motion of Suspended Particles in Glycerine and in Water.* *By* J. H. Smith, *M.Sc., Professor of Physics, Royal School of Engineering, Giza, Egypt* *.

SUSPENSIONS obtained with an iron arc under glycerine, prepared for some magnetic experiments, showed effects similar to those observed by Barkas in aqueous suspensions †. As these effects, attributed to photophoresis in the papers

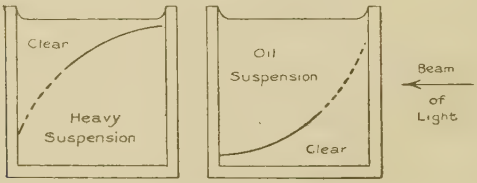
* Communicated by Prof. Alfred W. Porter, D.Sc., F.R.S.

† Phil. Mag. ii. p. 1019 (1926); and ix. p. 505 (1930).

cited above, seemed likely to interfere with the magnetic experiments, some tests were made on the effects of light alone.

The effects described by Barkas are indicated by fig. 1, which is taken from his second paper. Rectangular glass cells containing the suspensions were illuminated by a beam of light through one of the narrow vertical edges, and, after some time, a curved surface is formed by the cloud of particles which takes one of the forms shown in the figure. No marked difference in effect was produced by light passed through colour-filters. Similar effects were produced by a beam of X-rays, but not by the ultra-violet light from a mercury arc. Barkas made measurements of the velocities of separate particles in the suspensions, and concluded that particles of gold, silver, and gamboge, suspended in water, move against the light-beam, whilst particles of paraffin oil move in the same direction as the light-beam.

Fig. 1.



In most of the experiments described below the suspensions used were of iron in glycerine, the diameters of the largest particles being about ·05 mm. The smallest measured were about ·003 mm. The suspensions were contained in glass cells of dimensions $5 \times 2{\cdot}4 \times 1$ cm., and $4 \times 3{\cdot}5 \times 1$ cm. Using a 50-watt lamp as a source of transverse illumination, the suspensions, at 1 metre from the lamp, show the cloud curvature illustrated in fig. 1, both when a water-cell, 10 cm. in width, is placed between the lamp and the suspension, and also when the cell is removed. As might be expected, the action of the light on the suspension is quicker when the water-cell is removed. No change is observed in conformation when light polarized in different planes is used, and no effect of orientation is shown when the cloud pattern is viewed normally through crossed nicols. When the cloud was formed, an ordinary glass mirror, silvered on the back, was placed against the cell, on the side remote from the lamp, so as to reflect the light back along its path. This did not affect the cloud already formed.

It seems probable, therefore, that the effect of the absorption of light is to produce slow eddy currents. That these latter, produced by ordinary temperature differences, will produce this cloud curvature, was shown by exposing the edge of a cell to radiant heat from a copper vessel containing hot water. The cloud surface curves exactly as shown in fig. 1. When the edge of a cell was placed close to a pail containing ice the cloud curvature was again produced, the higher portion of the cloud being remote from the cold vessel, as might be expected. That the effects are not due to the glass was shown by immersing one end of a long copper strip vertically in the glycerine and heating the other end.

A cell containing pure glycerine was exposed to a light-beam, and after an hour's exposure at 50 cm. a crack appeared in the glycerine of the same shape as the cloud shown in fig. 1, continuing on long exposure in a D shape, reaching nearly to the bottom of the cell. The crack is easily photographed with the camera axis inclined at about 30° to the normal to the cell. Short pieces of unspun silk can be suspended in the glycerine. These show a velocity under the crack of the order of 1 cm. per minute in the direction which would be expected in a convection current. In weak suspensions of fine particles which will not settle, this crack is formed by transverse illumination, and coincides with the curved surface of the cloud.

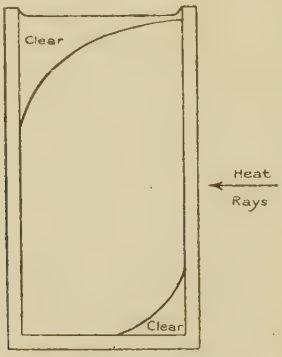
Velocity measurements were made in the iron suspensions, both on separate particles, and on pieces of silk introduced into the suspensions. The velocities varied from 2 cm. per minute to 0·02 cm. per minute. In all the cases observed the suspension seemed to be moving as a whole, there being no difference between the velocities of large and small particles in the same parts of the stream. Similar effects were observed in suspensions of fine silt in water and glycerine, and also in suspensions settling upwards, obtained by shaking up mineralized methylated spirit in water.

Measurements of temperature difference above and below the curved surfaces were made. The maximum difference for steady motion was about 1° C. and the minimum less than 0·05° C. In the experiments with pure glycerine described above the temperature difference above and below the crack is about 0·1° C.

The interesting fact is not the existence of the currents, but the fact that, in suspensions, the relative motion of two layers results in a transfer of particles normal to the direction of flow, so that, in the end, a stationary zone is denuded of

particles. When circulation is started in a suspension which has not begun to show a settling level, the first indication of the motion is the appearance of a swathe almost clear of particles, usually about 0·5 mm. wide, of the same shape as the cloud surface shown in fig. 1, and gradually extending down the liquid in the same way as the cloud surface does. The stagnant portion of the liquid gradually loses its suspended particles across this cleared zone, until the lower boundary of this zone becomes the cloud surface. When a descending cloud surface is formed before exposure to the light, as in Barkas's experiments, the boundary already formed limits the upward vertical current on the "light" side of the cell. When the vertical current extends, it carries the cloud boundary with it.

Fig. 2.



In the case of fine suspensions it is possible to get both the boundary forms of fig. 1 in the same suspension. This is shown in fig. 2, which is traced from a photograph.

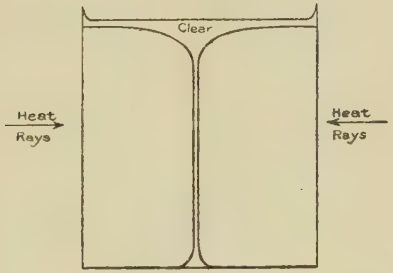
This progressive abstraction of stagnant zones is shown in another form in fig. 3, which shows a double circulation produced with two lamps, giving a vertical cleared zone with wide ends.

Similar effects are obtained when a metal cylinder, suspended centrally in a large cell containing a suspension, is heated by eddy currents. In the steady state all the particles are gathered into an inverted cardioid form. It is quite easy to map out the currents by observation of separate particles.

The particles appear to move through the liquid towards the places of maximum shear. Velocity measurements show

that there is very little shear in the moving portions, either in the suspensions or in the pure glycerine. In the latter case the lower boundary of the stagnant portion is in a semi-solid, In the case of a suspension settling under gravity the horizontal boundary of the suspension is a place of maximum shear, as the particles are far apart, and cannot therefore diminish the shear on one another; thus this semi-solid layer deflects the vertical currents set up by temperature differences. In a liquid each molecule acts as a surface to every other molecule, and viscosity is a measure of the time of association ; the energy difference between the associated and separate states is small, so that the probability of association is large. It is improbable that the field of force

Fig. 3.



of association is spherical, and in the cases described above it is possible that the boundary of a stagnant zone consists of chains of molecules nearly normal to the direction of flow of the adjacent liquid.

Summary.

Experiments are described, mainly on suspensions of iron in glycerine, which seem to show that cloud formations ascribed to the photophoresis of colloidal particles are probably due to very slow eddy currents, and that the effect of such currents is to denude the stagnant liquid of suspended particles. A similar boundary is produced by transverse heating in pure glycerine, the appearance of the boundary being that of a crack in thick glass.

III. *On a Study of the Upper Ionized Atmosphere in Bengal by Wireless Echoes of Short Delay.* By Prof. S. K .Mitra, *D.Sc., Khaira Professor of Physics, and* Hrishikesh Rakshit, *M.Sc., Khaira Research Scholar, Calcutta University* *.

[Plate III.]

Introduction.

IT is now generally recognized that there are two distinct ionized layers at different heights in the upper atmosphere which are responsible for the bending of the wireless waves down to the surface of the earth. The lower or the so-called E-layer, situated at an average height of about 80 km., is responsible for the propagation of long and medium waves and for night fading of broadcast signals. The upper or the F-layer, situated at an average height of about 250 km., is responsible for carrying short wave-signals round the earth. The two layers are quite distinct from one another and might be actually co-existent and are not, as is sometimes supposed, merely different locations of one and the same ionized layer which has moved continuously from one height to another. Very recently an interesting hypothesis has been put forward for explaining the co-existence of the two layers. It has been suggested that two distinct ionizing agencies are at work—one, the ultra-violet radiation from the sun, responsible for the lower E-layer and the other, the corpuscular radiation from the sun, responsible for the upper F-layer.

For some time past we have been engaged in studying the ionized upper atmosphere in the sub-tropical region of Bengal. A communication on this subject containing the results of an estimation of the height of the E-layer has already been published in this Journal [1]. In view of the importance of the subject it was decided to continue the study with especial reference to the heights of, and the echoes from, the upper F-layer. The results of our investigation and measurements are set forth in the present communication.

The observations were made with wave-lengths of 42, 50, 75, and 80 metres, and in the months of December 1931

* Communicated by the Authors.

and March, May, and June 1932. The transmissions were always made from the Wireless Laboratory at the University College of Science, and the power in the aerial seldom exceeded 20 watts. For observations in December and March the receiving station was permanently located at a distance of 3·8 km. from the College of Science. For the May to June observations the receiving apparatus was carried inside a small motor-bus and records were obtained at various distances and directions from the transmitter.

Experimental Method.

The method employed was the group retardation method as developed by Breit and Tuve [2]. Briefly it consists in sending out radio-frequency pulses or jabs of very short duration, and receiving the same at a moderate distance from the transmitter. The pulses reach the receiver by two distinct paths, one along the ground and the other " reflected " from the upper ionized atmosphere. The receiver thus records two pulses—one, the direct, and the other its echo—and from a knowledge of the time interval between the two, the equivalent height of the layer can readily be calculated.

The transmitter.—The original method of producing the pulses by Breit and Tuve did not give jabs of sufficiently short duration. Since the publication of their investigations various improvements on the production of the pulses have been made from time to time, and the method employed in the present investigation was the one originally suggested by Appleton and Builder [3]. Since the time interval between the signal and its echo is of the order of 1/1000 second, it is essential that the pulses should be of much shorter duration, not longer than 1/2000 or 1/3000 second, otherwise the signal and its echo might overlap in the recording system. Fig. 1 gives the diagram of the transmitter. The sharp interruptions in the oscillations produced are brought about by means of the diode D, the action of which has been explained by Appleton, Watt, and Herd [4]. For observations in December and March, with wave-lengths of 50 and 80 metres, the transmitting aerial system employed was of the inverted L-type with a counterpoise. During May to June observations with 42 and 75 metres,

the aerial system was changed over to the horizontal dipole type. The latter system of aerial gave much stronger echoes owing presumably to stronger radiation in the upward direction.

The recording system.—The recording system (fig. 2) consisted of two distinct parts—the receiver proper and the cathode ray oscillograph. The receiver had two stages of H.F. amplification followed by detection, and one stage of L.F. amplification. The cathode ray oscillograph had one pair of its deflecting plates connected to the output of the receiver, and the other pair to the output of the neon-tube oscillator for obtaining the

Fig. 1.

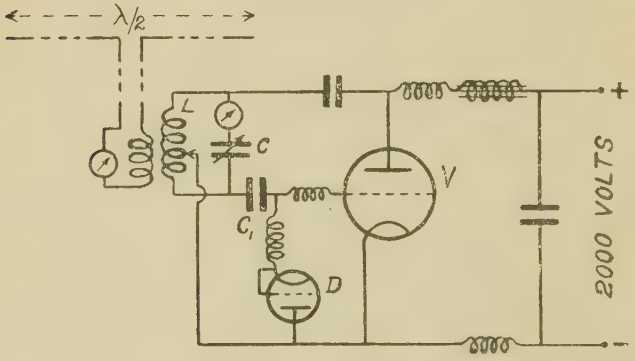


Diagram of transmitter ($\lambda = 42$ metres).

V—Phillips TB2/250. D—Phillips TC04/10. $C_1 = \cdot 025\mu F$.
$C = \cdot 0002\mu F$. $L = 4\mu H$.

linear time base. When the frequency of the time base oscillator is adjusted to the number of pulses produced per second at the transmitter, a steady pattern of the direct and of the several indirect signals is produced on the screen of the oscillograph. In order to maintain the synchronization, a small fraction of the pulsating energy from the output of the receiver is fed on to the circuit of the neon-tube oscillator by means of the condenser C, as shown in the figure. For observations with 50 and 80 metres the receiving aerial was of the ordinary outdoor inverted L-type, with a relatively

long horizontal portion. For 42 and 75 metres a single turn square frame aerial of side 90 cm. was used.

Measurement of height.

For a correct estimation of the equivalent height of the ionized layer it is essential to determine accurately the time interval between the direct and the indirect signal. It was found that the time base obtained from the neon-tube oscillator was far from linear. The time base was therefore calibrated by applying to the other pair of plates of the oscillograph a sinusoidal voltage, the frequency of which was a multiple of that of the time base. From the trace of the curve (Pl. III. fig. 2),

Fig. 2.

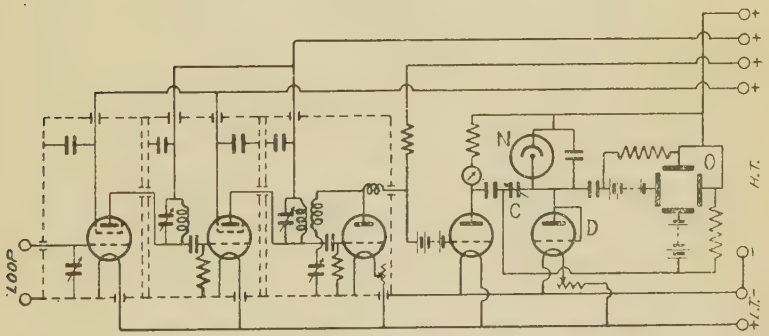


Diagram of the receiving and the recording system.

O—cathode ray oscillograph. N—neon tube. D—diode.
C—synchronizing condenser.

produced by the combination of the two oscillations, one could divide the time base into segments of gradually changing length, each segment corresponding to the same time interval, namely the period of the calibrating alternating voltage.

The measurement of the interval between the direct and the indirect signal was carried out both visually and photographically. A photographic record of a direct signal with two echoes is given in Pl. III. fig. 1. Very often sketches were made by hand of the relative intensities and positions of the multiple echoes by closely observing the pattern on the screen. For calculation

of the height, measurements of the interval made actually either on the screen or on the photograph were alone used.

As mentioned in the Introduction, the measurement of the height and other observations were made partly

TABLE I.

Date.	Time. h.	Time. m.	Wave-length in metres.	Height in kilometres.	Location of receiver with respect to transmitter. Distance (km.).	Direction
Mean sunset at ground 18 h. 06 m. 17.3.32.	12	00	50	264		
			80	No echo		
	16	00	50	240		
			80	240		
	18	30	50	208		
			80	208	3·8	N
Mean sunset at ground 18 h. 06 m. 21.3.32.	12	00	50	288		
			80	No echo		
	16	00	50	248		
			80	248		
	18	30	50	224		
			80	224		
Mean sunset at ground 18 h. 37 m. 2.6.32.	8	15	42	350	2·7	N
	8	30	„	350	2·4	W
	8	50	„	340	0·9	N
	9	00	„	345	0·5	N
	9	15	„	330	1·9	S
	9	30	„	330	1·4	E
	9	50	„	320	3·2	E

during December 1931 and March 1932 and partly during May and June 1932.

In the former case the recording system was permanently located at Cossipore, at a distance of 3·8 km. from the transmitter in a northerly direction. In the latter

case the recording apparatus was carried inside a small motor-bus and observations were made at different distances and directions from the transmitter within an area covered by a radius of 4 km. The transmissions were always made from the Wireless Laboratory at the University College of Science. Table I. gives a representative set of measured heights under various experimental conditions. It will be noticed from the table that the observed values of the heights do not change appreciably with the wave-length within the range studied. Particular attention was paid to detect any small variation of the measured height with change of wave-length. Arrangement was made by which the wave-length could be changed from 50 to 80 metres and *vice versa* within about five minutes, but, as stated above, no appreciable change in the height could be detected. It will also be noticed that neither the distance of the recorder from the transmitting station nor the direction in which the former is located has any bearing on the heights recorded on different days at different hours. The hour of observation, however, influences, in a marked degree, the measured heights. The height gradually decreases as the day proceeds, although the same height is not recorded at the same hour every day. The evening value is on the average lower by about 20 per cent. than the mid-day value on a particular day. It is difficult to draw any conclusion about the seasonal variation of the height. The measurements were made generally from the first echo from the F-layer and occasionally also from the second or the third echo. In every case the time interval between the direct and the second or the third echo was found respectively to be within the limits of experimental error, twice or thrice that between the direct signal and the first echo.

Occasionally echoes were obtained towards the afternoon from the lower E-layer. They were generally very feeble. The height calculated from our records had an average value of about 70 km. There was no correlation between the height corresponding to this echo and that corresponding to the single or multiple echoes described above. The measured height of this E-layer agrees well with our previous observations [1] made with broadcast waves.

Multiple Echoes.

One of the most remarkable features of the echoes is their multiplicity, which is very conspicuous near about sunset. Instead of one reflected signal, one records a number of such signals—sometimes as many as six. We observed in some detail the multiplicity, and the results of our observations are briefly summarized here.

1. The multiple echoes begin to be noticed from about one hour before sunset and last till about half an hour after sunset. This feature is common for all the wave-lengths employed, viz., 42, 50, 75, 80 metres. Multiple echoes are also observed during day-time, but their number and intensities are both very small as

TABLE II.

Distance in kilometres.	Number of echoes.	Relative intensities.		
		F_1.	F_2.	F_3.
0·2	nil	—	—	—
0·4	1	very weak	—	—
1·0	2	weak	very weak	—
1·6	2	weak	very weak	—
2·0	3	medium	very weak	very weak
3·0	3	strong	weak	very weak

compared with those observed near the sunset period. During the day time we were seldom able to observe more than two echoes. Only occasionally a very feeble third echo could be seen. The intensities of the echoes are never steady but always undergo rapid fluctuations, the change from a maximum to a minimum occurring sometimes within one or two seconds.

2. We have invariably found that the number of echoes increases as one moves away from the transmitter. A typical set of observations is given in Table II. to show how the number of echoes increases with distance.

It will be seen from the table that the echoes first begin to be perceptible from a distance of about half

a kilometre. This is generally true for the afternoon. In the morning one has generally to move away about one kilometre before one notices the first echo. A faint trace of this echo is, however, occasionally obtained between a half and one kilometre, but it is neither so persistent nor so strong as that obtained in the afternoon. The number of echoes at a distance of 3 km. is shown as three, but in the afternoon they might increase to five or six. Such large numbers of echoes are, however, never observed when one is within a range of one kilometre from the transmitter. The intensities of the successive echoes have been shown as gradually diminishing. In the afternoon, however, the echoes show anomalous variations of intensities, to which reference will be made later. Considering the small distance (only 3 or 4 kilometres) over which one has to move in order to obtain an increase in the number of echoes, the phenomenon certainly seems strange. If the reflecting layer is supposed to be horizontal, the incidence of the rays is practically vertical for all the reflected rays within the small distance surveyed. Remembering that the reflecting layer is situated at an equivalent height of about 250 km. one would expect that if it were possible to detect echoes at a distance of half a kilometre from the transmitter, it would also be possible to detect them even right under the transmitter for absolutely normal incidence. And further, their number and relative intensities ought not to vary in any marked degree when one shifts the point of observation from place to place within a radius of 4 or 5 km. round the transmitter. The table, which is a typical one taken at random from a set of very large number of observations on different dates, unmistakably shows that :

(*a*) the number of echoes increases with distance ;

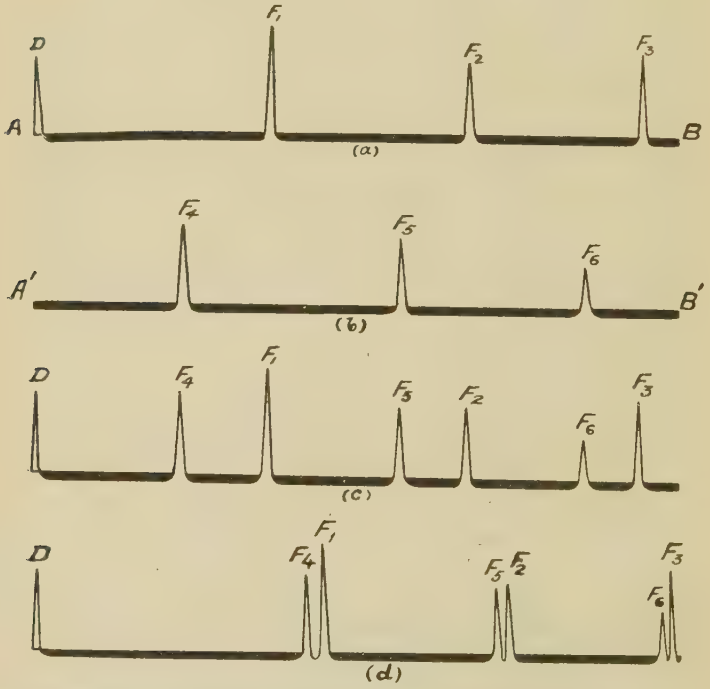
(*b*) the intensity of first reflected ray always increases, as one moves away from the transmitter over the small distance of 3 or 4 km.

3. The interval between the successive echoes has been found to be constant within the limits of experimental error. This confirms the hypothesis that the multiple

echoes are due to multiple reflexion between the earth and F-layer. The proof of the absolute equality of the time intervals has also been obtained in an interesting manner, without actual measurement, from the observations described below.

When experimenting with 42 metres wave-length the period of the time base was such that it could not contain more than three echoes. In fig. 3 (*a*) and (*b*),

Fig. 3.



Illustrating the overlapping of echoes of higher orders on those of lower orders. In (*c*) and (*d*) the intervals F_4, F_1, etc., do not appear equal since the time base was not quite linear.

AB and A′B′ represent two successive traces of the time base on the screen of the cathode ray oscillograph (they are of course coincident but have been shown separately). AB or A′B′ represents 1/150 second, which, neglecting the small time (1/4000 sec.) taken by the spot

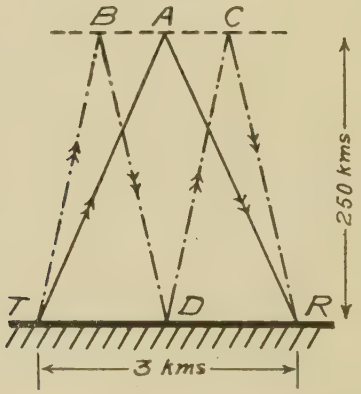
to travel back from A to B, is the same as the period of the interruptions at the transmitter. D, F_1, F_2, F_3 represent respectively the upward strokes of the cathode ray spot due to the direct, the once, the twice, and the thrice reflected signals from the F-layer. Actual measurements show that the intervals DF_1, F_1F_2 and F_2F_3 are all equal, and for the average height measured is equal to about 1/500 second. The interval DF_3 is thus nearly equal to that between A and B.

If now there be signals reflected four, five or six times, they cannot evidently be contained between F_3 and B, but they (F_4F_5, etc.) will rather be formed in the next trace A′B′ of the time base. The interval F_3B together with $A'F_4$ is equal to AF_1; F_4F_5, F_5F_6 have also the same value. (It may be remarked that the difference of the intervals F_1F_4 and F_3B gives the time taken by the cathode ray spot to travel back from B to A.) The totality of the echoes F_1, F_2, ... F_6 will therefore appear as depicted in fig. 3 (*c*). This apparent doubling of the echoes has actually been observed on many occasions towards the afternoon. By slight adjustment of the frequency of the transmitted pulses, together with a corresponding adjustment of the period of the time base, the relative positions of F_1, F_2, F_3 with respect to F_4, F_5, F_6 can be varied in any manner. For instance, F_4, F_5, F_6 might be made to fall midway between DF_1, F_1F_2, and F_2F_3; or, if so desired, they can be made nearly coincident with F_1, F_2, and F_3 respectively. This latter case is depicted in fig. 3 (*d*). This proves that the time interval between successive echoes is exactly the same.

4. A curious fact noticed about the multiple echoes is the absence of any regularity in their relative intensities. Assuming the surface of the earth and the ionized layer to be perfect reflectors, one would expect the intensities of the successive echoes to diminish inversely as n^2 where n is equal to 1, 2, 3, etc., for the once, twice, thrice, etc. reflected echoes, since the distances traversed by the successive echoes are in the ratio of 1 : 2 : 3, etc. But instead of such a gradual falling-off of intensity in accordance with the inverse square law, one frequently observes an echo of higher order having an intensity much greater than one of a lower order. This anomaly

is especially noticeable towards the afternoon and in the echoes of the lower orders—a typical case being the second echo much stronger than the first. A satisfactory explanation of this curious feature of the echoes is not easy to find. An explanation which naturally suggests itself is that echoes of different orders are returned from different " points " of the ionized layer and these points might have different " reflectivities." For instance, the points B, C (fig. 4) struck by the twice reflected ray might be better reflectors than the point A struck by the once reflected ray. This might cause the intensity of the twice reflected ray to be much greater than that

Fig. 4.



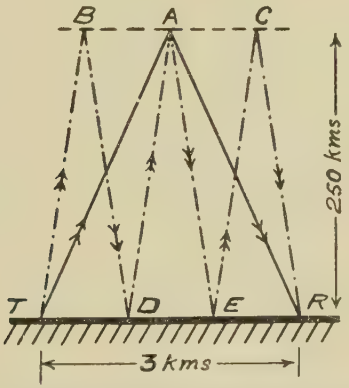
Illustrating once and twice reflected rays between the ground and the ionized layer. T, transmitter. R, receiver.

of the once reflected one. This explanation receives support when one compares the intensities of the once and thrice reflected echoes. From fig. 5 it will be seen that the once and the thirce reflected rays have one common reflecting point at A. The intensities of the once and the thrice reflected rays being both dependent on the reflecting power of the point A, the thrice reflected ray can never be stronger than the once reflected one even if the the points B, D, E, and C behave as perfect reflectors. This is what we have actually observed. None of our records, nor any of those of previous workers,

show the thrice reflected ray stronger than the once reflected one, though very frequently the twice reflected is many times stronger than the once reflected. There is another point in favour of the above hypothesis. From fig. 5 it is evident that according to this hypothesis the first reflected ray at D must be stronger than the second reflected one observed at R—this is what has been repeatedly observed.

The actual manner in which the "reflectivity" of the ionized layer changes so rapidly from point to point and within such short intervals is, however, difficult to explain. Also, there must be enormous point to point

Fig. 5.



Illustrating once and thrice reflected rays between the ground and the ionized layer. T, transmitter. R, reviver.

variation in the reflecting power when one observes an echo of a higher order stronger than one of a lower order. The higher order echo has suffered loss in strength according to the inverse square law for having travelled a greater distance and also for having undergone earth reflexion. One has to conclude, therefore, that these losses are more than compensated by the greater reflecting power of the points from which the higher order echo is returned from the ionized layer. More detailed observations are needed before any satisfactory explanation can be given of the anomalous variation of the intensities of the multiple echoes.

Summary and Conclusion.

The height of the upper ionized F-layer has been measured in Bengal with wave-lengths of 42, 50, 75, and 80 metres. No marked variation in the measured height is observed with change of wave-length within the range studied. The height, however, changes with the season of the year and the hour of the day. The average height has a value of 250 km. in the afternoon. The evening value is lower by about 20 per cent. than the midday value on any particular day.

The multiplicity of the echoes has been observed in some detail. The hour of its most frequent occurrence is during sunset period. By overlapping echoes of higher orders on those of lower orders (as seen on the screen of the oscillograph) it has been proved that the time interval between the successive echoes is accurately constant. This supports the hypothesis that multiple echoes are caused by multiple reflexion between the earth and the ionized layer.

The intensities of the successive echoes do not apparently follow any regularity. It has been found, however, that a thrice reflected echo is never stronger than a once reflected one. The probable causes of such anomalies in the intensities of the echoes of different orders are discussed.

We desire to express our thanks to the authorities of the Indian State Broadcasting Service for having allowed us the exclusive use of a room at the transmitting station at Cossipore during the first part of our observations.

References.

(1) Phil. Mag. xii. p. 897 (1931).
(2) Phys. Rev. xxviii. p. 554 (1926).
(3) Nature, June 27, p. 970 (1931).
(4) Proc. Roy. Soc. cxi. p. 672 (1926).

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IV. *Gravitation and Electricity.*—Part II.

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1. In the paper which preceded the present one, it was shown that certain modified forms, which have been suggested for Maxwell's classical theory of electromagnetism, indicate the possibility of formulating a field theory of a very general type. In this a tensor H_{jk}, defined as the generalized force tensor of the field, is split into its anti-symmetrical and symmetrical parts F_{jk}, G_{jk}; the first of these is the ordinary force tensor of electrodynamic theory, and the second—a force of a somewhat different type—is regarded as having its origin in the gravitational field, and as a force acting on the matter in the field more or less as the anti-symmetric tensor represents a force acting on the charge. In this way it seemed possible to formulate a simple unified field theory independently of the general discussions of the theory of relativity.

Further, it was emphasized that this theory is closely connected with certain suggestions made both in Eddington's 'Affine Geometry †' and in the later forms of Einstein's 'Unified Field Theory ‡.'

2. In the present paper we shall attempt to give a satisfactory mathematical formulation of the theory in its most general form, and this we shall do by means of variational principles. Ordinary dynamical methods involving the Principal of Least Action will be first employed. Then, in order to confirm the validity of the results so derived and to establish them still further, we shall combine with this method of varying the independent field functions which define the physical configurations of the system the newer method of transforming the coordinate system. This latter method, which arose in connexion with certain discussions associated with Einstein's 'Gravitational Theory' of 1915, involves a general infinitesimal transformation of the space-time coordinate system (the dynamical system remaining fixed or unchanged in the physical or natural world), and it is therefore fundamentally different from the old method

* Communicated by Prof. G. H. Livens, M.A.

† Proc. R. S. A, xcix. p. 104 (1921), and 'Mathematical Theory of Relativity,' pp. 213–240 (1923).

‡ *Sitz. d. Preuss. Akad.* i. pp. 18–23 (1930), and Math. Ann. cii. pp. 685–697 (1930).

of variation, wherein the system defined by its physical coordinates is made to undergo a slight distortion in a fixed coordinate frame of reference. Our analysis will be given throughout in the now familiar four-dimensional symmetrical form, with the usual conventions of the tensor calculus.

3. If F_{jk} is the second-order anti-symmetric tensor (with components H_x, H_y, H_z, iE_x, iE_y, iE_z) defining the electromagnetic field, then the action integral of this field expressed in the usual notation is :

$$\frac{1}{2}\int F_{jk}^2 dx = \frac{1}{4}\int F_{jk}\,F_{jk} dx,$$

in terms of Heaviside-Lorentz units so that the 4π factor disappears. For the gravitional field we shall, therefore, assume

$$-\frac{1}{4}\int G_{jk}\,G_{jk} dx,$$

so that for the complete field,

$$A = \frac{1}{4}\int (F_{jk}\,F_{jk} - G_{jk}\,G_{jk}) dx.$$

We cannot vary independently the quantities F_{jk}, G_{jk}, in our integral unless other invariant relations connecting them with the real physical coordinates, the position coordinates of the charges giving rise to the field, are introduced into the integrand.

Now it has been shown in electromagnetic theory that, if the equations of Gauss and Ampere are assumed as conditions governing the variation, then Faraday's equations are derived as a result of the variational process, together with the equations of motion of the charge elements. Thus, in four-dimensional (Galilean) notation, the action integral for the electromagnetic field is proposed in the form

$$\int \left\{ \left(\tfrac{1}{4} F_{jk}\,F_{jk} - \phi_j \frac{\partial F_{jk}}{\partial x_k} \right) + \phi_j s_j \right\} dx,$$

the ϕ's being undetermined multipliers and

$$dx = dx_1, dx_2, dx_3, dx_4.$$

Corresponding to this for gravitational fields we shall, following the suggestions contained in the paper to which this forms a sequel, interpose the relations

$$\frac{\partial G_{jk}}{\partial x_k} = -t_j, \quad \ldots\ldots \quad (1)$$

in the action integral as equations of condition, and then the integral in its modified form becomes

$$-\int\left\{\left(\tfrac{1}{4}G_{jk}\,G_{jk}-\phi_j'\frac{\partial G_{jk}}{\partial x_k}\right)-\phi_j' t_j\right\}dx.$$

The quantities ϕ_j, ϕ_j' introduced here, are Lagrangian undetermined functions of the coordinates, and the vectors s_j, t_j are defined by

$$s_j=\rho v_j, \qquad t_j=\rho' v_j,$$

where ρ is the electric charge density, and ρ' the density of the gravitational mass, of a small element of volume of the field which is moving with velocity v_j $(=v_x,\ v_y,\ v_z,\ i)$. Finally, then, for the unified field we have

$$\int\left\{\tfrac{1}{4}(F_{jk}F_{jk}-G_{jk}G_{jk})-\left(\phi_j\frac{\partial F_{jk}}{\partial x_k}-\phi_j s_j-\phi_j'\frac{\partial G_{jk}}{\partial x_k}-\phi_j' t_j\right)\right\}dx.$$

From this we shall be able to secure a knowledge of the remaining field laws by varying the F_{jk} and G_{jk}, which can now be considered as independent functions of the system.

4. In the present discussion, we shall confine our attention to those terms in the unified action integral which depend on the G field alone; or, in other words, we consider a purely gravitational field by carrying out the variation of

$$A_G \equiv -\int\left\{\tfrac{1}{4}G_{jk}\,G_{jk}-\phi_j'\left(\frac{\partial G_{jk}}{\partial x_k}+t_j\right)\right\}dx.$$

This field alone is described here because the corresponding analysis for an electromagnetic field—namely, the variation of

$$A_F \equiv \int\left\{\tfrac{1}{4}F_{jk}\,F_{jk}-\phi_j\left(\frac{\partial F_{jk}}{\partial x_k}-s_j\right)\right\}dx,$$

would provide us only with results with which we are already familiar in Maxwell's Theory and, in any case, it is practically identical in form with that which is to be given.

As usual in problems of the present type, we need not concern ourselves with terms at the limits of integration, and then the variation of A_G is equal to

$$-\int\left(\tfrac{1}{2}G_{jk}+\frac{\partial\phi_k'}{\partial x_j}\right)\delta G_{jk}dx.$$

But the variations δG_{jk} can now be considered as independent

and arbitrary, and hence the coefficient of each in the above must vanish separately. We thus obtain the set of equations:

$$\tfrac{1}{2}G_{jk}+\frac{\partial\phi_k'}{\partial x_j}=0$$

or

$$G_{jk}=-\left(\frac{\partial\phi_k'}{\partial x_j}+\frac{\partial\phi_j'}{\partial x_k}\right).$$

By analogy with Electromagnetic Theory, the four undetermined functions ϕ_j' will be described as constituting the "potential" vector of a gravitational field; but it must be stressed that these "potentials" introduced at first merely as auxiliary mathematical functions—the undetermined multipliers—still remain as such, and have no direct physical significance. (The same is true of the "potentials" of electromagnetism.)

5. Relations which are practically the equations of motion of the individual mass particles in the system can be obtained by including in the Lagrangian function a term which depends solely on the particles themselves. The variation then has also to include variations of the vectors defining the positions of the particles. For the action integral is taken, then

$$\int L_0 ds-\int\left\{\tfrac{1}{4}G_{jk}G_{jk}-\phi_j'\frac{\partial G_{jk}}{\partial x_k}\right\}dx-\int\{\phi_j' t_j\}ds,$$

where $\int L_0 ds$ is an intrinsic Lagrangian function of the type described above, and the components of t_j are given by

$$(t_1, t_2, t_3, t_4)=\Sigma m_0\left(\frac{dx}{ds}, \frac{dy}{ds}, \frac{dz}{ds}, i\frac{dt}{ds}\right),$$

the summations being taken over all the individual mass particles within the small element of volume considered. [s is the "proper" time and m_0 the "proper" mass (inertial) of a typical particle which is moving with velocity $v=\left(\frac{dx}{dt}, \frac{dy}{dt}, \frac{dz}{dt}\right)$.] The element is given a virtual displacement $\delta_0 x_j$, and the coefficients of $\delta_0 x_j$ in the expression thus derived from A_G equated to zero in order to obtain the force which is required. It is only the first and last terms in the action integral, however, which contribute to the total

value of this variation since only these refer to the motion of the individual particles inside the volume element.

The variation of $\int L_0 ds$ gives

$$\int \left\{ \frac{\partial L_0}{\partial x_k} - \frac{d}{ds}\left(\frac{\partial L_0}{\partial \dot{x}_k}\right) \right\} \delta_0 x_k ds \qquad \left(\dot{x}_k \equiv \frac{dx_k}{ds}\right),$$

and the variation of

$$\int \phi_j' t_j ds \equiv \int \phi_j' \left(\Sigma m_0 \frac{dx_j}{ds}\right) ds$$

gives

$$\begin{aligned}
&\int \left\{ \phi_j' \Sigma m_0 \frac{d \cdot \delta_0 x_j}{ds} + \Sigma m_0 \frac{\partial \phi_j'}{\partial x_k} \delta_0 x_k \frac{dx_j}{ds} \right\} ds \\
&\quad = \int \left\{ -\frac{\partial \phi_j'}{ds} \Sigma m_0 \delta_0 x_j + \Sigma m_0 \frac{\partial \phi_j'}{\partial x_k} \cdot \frac{dx_j}{ds} \delta_0 x_k \right\} ds \\
&\quad = \int \left\{ -\Sigma m_0 \frac{\partial \phi_j'}{\partial x_k} \frac{dx_k}{ds} \delta_0 x_j + \Sigma m_0 \frac{\partial \phi_k'}{\partial x_j} \frac{dx_k}{ds} \delta_0 x_j \right\} ds \\
&\quad = \int \Sigma m_0 \left(\frac{\partial \phi_k'}{\partial x_j} - \frac{\partial \phi_j'}{\partial x_k} \right) \frac{dx_k}{ds} \delta_0 x_j ds \\
&\quad = -\int F'_{kj} t_k \delta_0 x_j ds,
\end{aligned}$$

where $$F'_{kj} = -\left(\frac{\partial \phi_k'}{\partial x_j} - \frac{\partial \phi_j'}{\partial x_k}\right).$$

(We have assumed again that all surface integrals vanish.) Hence, for the total variation we have

$$\int \left[\left\{ \frac{\partial L_0}{\partial x_k} - \frac{d}{ds}\left(\frac{\partial L_0}{\partial \dot{x}_k}\right) \right\} + F'_j t_j \right] \delta_0 x_k ds.$$

But the variations $\delta_0 x_k$, which determine the virtual displacement of the volume element, are independent of one another and of all other variations of the field functions, and therefore we have

$$\frac{d}{ds}\left(\frac{\partial L_0}{\partial \dot{x}_k}\right) - \frac{\partial L_0}{\partial x_k} = F_{kj}' t_j.$$

These equations show that

$$F_k' \equiv F'_{kj} t_j = -\left(\frac{\partial \phi_k'}{\partial x_j} - \frac{\partial \phi_j'}{\partial x_k}\right) t_j,$$

is the gravitational force acting on this small volume element which contains individual mass particles.

It thus appears that the forcive in the gravitational field is defined in terms of the anti-symmetrical tensor:

$$-\left(\frac{\partial \phi_k'}{\partial x_j}-\frac{\partial \phi_j'}{\partial x_k}\right);$$

this fact must be emphasized, for we might have expected that it would be of the symmetrical form

$$-\left(\frac{\partial \phi_k'}{\partial x_j}+\frac{\partial \phi_j'}{\partial x_k}\right)t_j=\mathrm{G}_{jk}t_j,$$

since the corresponding expression in electrodynamics is

$$-\left(\frac{\partial \phi_k}{\partial x_j}-\frac{\partial \phi_j}{\partial x_k}\right)s_j=\mathrm{F}_{kj}s_j.$$

6. We have now specified the field equations, and the forcive on an element of mass, but before we can consider our formulation of the gravitational field complete, we must attempt, as in electromagnetic theory, to express the above forcive as derived from a four-dimensional stress-energy tensor of the mass field. That is, we shall hope to show that the forcive F_k' can be written in the form

$$\mathrm{F}_k'=-\frac{\partial \mathrm{T}_{kj}}{\partial x_j}.$$

Making use of the set of field equations

$$\frac{\partial \mathrm{G}_{jp}}{\partial x_p}=-t_j,$$

we have

$$\mathrm{F}_k'\equiv \mathrm{F}'_{kj}t_j=-\mathrm{F}'_{kj}\frac{\partial \mathrm{G}_{jp}}{\partial x_p}=\frac{\partial}{\partial x_p}(\mathrm{F}'_{kj}\mathrm{G}_{jp})+\frac{\partial \mathrm{F}'_{kj}}{\partial x_p}\mathrm{G}_{jp},$$

and now, substituting for F_{kj} in terms of the functions ϕ_k', we have further:

$$\begin{aligned}\mathrm{F}_k' &= -\frac{\partial}{\partial x_p}(\mathrm{F}'_{kj}\mathrm{G}_{jp})+\mathrm{G}_{jp}\frac{\partial \mathrm{G}_{kj}}{\partial x_p}+2\mathrm{G}_{jp}\frac{\partial^2 \phi_j'}{\partial x_k\,\partial x_p}\\ &= -\frac{\partial}{\partial x_p}(\mathrm{F}'_{kj}\mathrm{G}_{jp})+\frac{\partial}{\partial x_p}(\mathrm{G}_{jp}\mathrm{G}_{jk})-\tfrac{1}{2}\mathrm{G}_{jn}\frac{\partial \mathrm{G}_{jn}}{\partial x_k}\\ &\quad +2\mathrm{G}_{ip}\frac{\partial^2 \phi_j'}{\partial x_k\,\partial x_p}\\ &\quad +\mathrm{G}_{jk}t_j+\tfrac{1}{2}\mathrm{G}_{jp}\frac{\partial \mathrm{G}_{jp}}{\partial x_k}\end{aligned}$$

$$= \frac{\partial}{\partial x_p}(-\mathrm{F'}_{jk}\mathrm{G}_{jp} + \mathrm{G}_{jp}\,\mathrm{G}_{jk}) - \tfrac{1}{4}\frac{\partial}{\partial x_p}(\mathrm{G}_{jn}\,\mathrm{G}_{jn}\delta_{kp})$$
$$+ \mathrm{G}_{jk}t_j + \mathrm{G}_{jn}\left[\frac{\partial^2\phi_j'}{\partial x_k\,\partial x_p} - \tfrac{1}{2}\left(\frac{\partial^2\phi_j'}{\partial x_k\,\partial x_p} + \frac{\partial^2\phi_p'}{\partial x_k\,\partial x_j}\right)\right]$$
$$+ \frac{\partial}{\partial x_p}\left(\mathrm{G}_{jp}\frac{\partial\phi_j'}{\partial x_k}\right) + \frac{\partial\phi'}{\partial x_k}t$$
$$= \frac{\partial}{\partial x_p}\left[-\mathrm{G}_{jp}\frac{\partial\phi_j'}{\partial x_k} - \tfrac{1}{4}\mathrm{G}_{jn}\,\mathrm{G}_{jn}\delta_{kp}\right] - t_j\frac{\partial\phi_k'}{\partial x_j}$$
$$= -\frac{\partial}{\partial x}\left[\tfrac{1}{4}\mathrm{G'}_{jn}\,\mathrm{G}_{jn}\delta_{kp} + \mathrm{G}_{jp}\frac{\partial\phi^{jl}}{\partial x_k} + t_p\phi_k'\right]$$
$$= \frac{\partial \mathrm{T}_{kp}}{\partial x_p},$$

where

$$\mathrm{T}_{kp} = -\left[\tfrac{1}{4}\mathrm{G}_{jn}\,\mathrm{G}_{jn}\delta_{kp} + \mathrm{G}_{jp}\frac{\partial\phi_j'}{\partial x_k} + t_p\phi_k'\right].$$

This tensor T_{kp}, which has been constructed so that the forcive F_k' is given by

$$\mathrm{F}_k' = \frac{\partial \mathrm{T}_{kp}}{\partial x_p},$$

is therefore the required stress energy tensor of the theory, and thus completes the specification of the general relations of our theory.

Nowadays, however, it is more usual to show these stress energy relations as conditions for the invariance of the action integral, and as this is perhaps a more direct method of deriving them in any case, it seems desirable to give this derivation formally, especially as certain new and important features connected with the method have emerged. To do this we must, however, generalize the theory to the form in which it holds in all coordinates—Galilean and otherwise. We shall, therefore, take the most general case of a space defined by the general metric :

$$ds^2 = g_{jk}dx^j dx^k,$$

the particular results obtained above being then derivable by putting

$$g_{jk} = g^{jk} = \delta_j^{\,k} = 1 \quad \text{if } j = k$$
$$= 0 \quad \text{if } j \neq k.$$

We shall presently carry out this transformation, but it

seems necessary first to give a brief account of the development and general character of this method of variation to be employed which is essentially an invariant method of the Calculus of Variations.

7. *An infinitesimal transformation of the coordinate system* *. Suppose that the coordinate system x_i is subject to a transformation defined by

$$x_i' = x_i + \epsilon\xi^i(x),$$

where ϵ is an infinitesimally small quantity of which all powers higher than the first will be neglected; $\xi^i(x)$ are arbitrary functions of the coordinates. The components of any tensor in terms of the new coordinates are given by the usual formula:

$$T'^{k_1 \dots k_r}_{l_1 \dots l_s} = T^{a_1 \dots a_r}_{b_1 \dots b_s} \frac{\partial x'^{k_1}}{\partial x_{a_1}} \cdots \frac{\partial x'^{k_r}}{\partial x_{a_r}} \cdot \frac{\partial x_{b_1}}{\partial x'_{l_1}} \cdots \frac{\partial x_{b_s}}{\partial x'_{l_s}}.$$

But now,

$$\frac{\partial x_i'}{\partial x_a} = \delta_a^{\ i} + \epsilon \frac{\partial \xi^i}{\partial x_a}$$

and since

$$\frac{\partial x_i'}{\partial x_a} \cdot \frac{\partial x_a}{\partial x_k'} = \delta_k^{\ i},$$

we have (neglecting squares and higher powers of ϵ),

$$\frac{\partial x_a}{\partial x_i'} = \delta_a^{\ i} - \epsilon \frac{\partial \xi^i}{\partial x_a},$$

and also

$$\left|\frac{\partial x_i'}{\partial x_k}\right| = 1 + \epsilon \frac{\partial \xi^i}{\partial x_i}, \qquad \left|\frac{\partial x_k}{\partial x_i'}\right| = 1 - \epsilon \frac{\partial \xi^i}{\partial x_i},$$

wherein the reappearance of the same index i implies summation over the n coordinates, as in the ordinary convention of the Tensor Calculus, which will now be in use generally. Hence, for the infinitesimal transformation of the coordinates

$$T'^i = T^a\left(\delta_a^{\ i} + \epsilon \frac{\partial \xi^i}{\partial x_a}\right),$$

and, therefore, the resulting variation of the vector is given by:

$$\Delta T^i = \epsilon \frac{\partial \xi^i}{\partial x_a} T^a.$$

* Weyl, *Ann d. Physik.* liv. pp. 122–124 (1917); Pauli, *Encykl. d. Math. Wissen.* Bd. V. ii. Art. 19, pp. 616–622 (1920).

Similarly,

$$\Delta T_i = -\epsilon \frac{\partial \xi^a}{\partial x_i} T_a,$$

and the variations of tensors of the second degree are determined according to

$$\Delta T^{ik} = \epsilon \left(\frac{\partial \xi^i}{\partial x_a} T^{ak} + \frac{\partial \xi^k}{\partial x_a} T^{ia} \right),$$

$$\Delta T_{ik} = \epsilon \left(\frac{\partial \xi^a}{\partial x_i} T_{ak} + \frac{\partial \xi^a}{\partial x_k} T_{ia} \right),$$

$$\Delta T_k^{\ i} = \epsilon \left(\frac{\partial \xi}{\partial x_a} T_k^{\ a} - \frac{\partial \xi^a}{\partial x_k} T_a^{\ i} \right).$$

In particular, of course, these formulæ apply to the variations of the fundamental metric tensor g_{ik}.

The variations considered above are given by

$$\Delta T_r = T_r'(x') - T_r(x)$$

and

$$\Delta T_{ik} = T'_{ik}(x') - T_{ik}(x).$$

But now let δ denote the variation which a tensor quantity undergoes *at a fixed point* x—the covariant variation. Then:

$$\begin{aligned} \delta T_r - \Delta T_r &= \{T_r'(x) - T_r(x)\} - \{T_r'(x') - T_r(x)\} \\ &= -\{T_r'(x') - T_r'(x)\} \\ &= -\epsilon \xi^s \frac{\partial T_r}{\partial x_s}, \end{aligned}$$

or, generally,

$$\delta = \Delta - \epsilon \xi^i \frac{\partial}{\partial x_i}.$$

8. Let us now examine the variation produced by such an infinitesimal transformation of the coordinates, in a multiple integral form of n independent variables $x_1 \ldots x_n$; namely,

$$I = \int_{x_1} \ldots \int_{x_n} A \, dx_1 \ldots dx_n,$$

where I is an invariant, and therefore A a scalar density. For brevity, this integral is denoted by

$$I = \int_x A \, dx,$$

and its total variation, then, is given by

$$\begin{aligned}\Delta I &= \Delta \int_x A(x)dx \\ &= \int_{x^1} A'(x')dx' - \int_x A(x)dx \\ &= \int_x A'(x') \left|\frac{\partial x_i'}{\partial x_k}\right| dx - \int_x A(x)dx,\end{aligned}$$

and since

$$A'(x') = A'(x) + \epsilon\xi^i \frac{\partial A(x)}{\partial x_i},$$

$$\delta A(x) = A'(x) - A(x),$$

therefore, the complete variation of the integral is equal to

$$\begin{aligned}\Delta \int_x A(x)dx &= \int_x \left[\delta A(x) + \epsilon \frac{\partial}{\partial x_i}\{A(x)\xi^i\}\right] dx \\ &= \int_x \delta A(x)dx + \epsilon \left|\int \{A(x)\xi^i\} dX_i\right|,\end{aligned}$$

the last term denoting n integrals of order $n-1$, since partial integration with respect to x_i has already been effected. [It may be noted that, for a general infinitesimal coordinate transformation of the type under discussion, the g_{ik} are restricted to conform to the law

$$\Delta \int ds \equiv \Delta \int \sqrt{(g_{ik}\, dx_i\, dx_k)} = 0.]$$

After the expressions for the covariant variations of the field tensors have been substituted in $\delta A(x)$, conservation principles are obtained for the system corresponding to the values of ξ^i, for possible infinitesimal transformations of the coordinates conforming to the above condition. We shall, however, always take $(\epsilon\xi^i)$ to be constants, and then we must express the condition that the variation is to vanish for arbitrary ξ^i. It will be seen that these simple special values for ξ^i in the four-dimensional variation of the invariant action integral of a continuous system are sufficient to derive, and in fact are those which give the equations of energy and momentum of the system.

9. For a four-dimensional space, variations of integrals of the type

$$\int \sqrt{(-g)}\, A\, dx_1\, dx_2\, dx_3\, dx_4 = \int \sqrt{(-g)}\, A\, dx,$$

will have to be considered, and we shall now apply this method of variation to the case of a gravitational field with action integral

$$\frac{1}{4}\int G_{ik}G_{ik}dx,$$

which becomes

$$\frac{1}{4}\int\sqrt{(-g)}G^{ik}\,G_{ik}dx* \equiv \frac{1}{4}\int \mathbf{G}^{ik}\,G_{ik}dx,$$

in invariant tensor form, wherein we have written

$$\mathbf{G}^{ik}\equiv\sqrt{(-g)}G_{ik},$$

g being, of course, the value of the determinant $|g_{ik}|$. Before, however, proceeding with the analytical development of this problem, let us pause for a moment to examine the principles involved and to ascertain, if possible, what information we may expect to obtain from the process.

The integral which we propose to vary has been constructed in such a way that it is completely invariant in form. The analysis amounts, therefore, to an estimation of the total variation of an *a priori* invariant integral consequent upon an infinitesimal tranformation of the coordinate system. The resultant variation must therefore be identically zero since an invariant is, by definition, unaffected in value by any change of coordinates. It follows, then, that the integral part and the sum of all the limit terms which appear in the variation must vanish identically. By considering the various possibilities of independence between the different variations of the coordinates the integral part of the expression gives, as above, certain identities (conservation laws) equal in number to the number of possible independent variations. What, then, do the limit terms give? In previous applications of this analysis it has been usual to ignore these limit terms, or at least to make them ignorable by assuming that the variations of all independent functions are restricted so as to vanish at the boundaries. One of us † found, however, in attempting an evaluation of the terms in the electrodynamic case, that all these limit terms do automatically vanish identically, without any special assumptions as to the behaviour of the variations on the boundary, so that they are of no real concern in the problem before us. We shall, therefore, always omit the limit terms at all stages of the

* The negative sign is used here and always under this radical sign since, for real coordinates, g is always negative.

† Dr. Viney, and the result has been confirmed subsequently in the more general case.

variational process, leaving it to the reader to verify our statement that they are identically zero.

10. Returning, then, to our variational problem itself, let us carry out the general variation of our multiple integral, combining with the result obtained by space variation also the ordinary results obtained by varying the independent field functions.

We cannot, of course, vary independently the G_{ik}, g_{ik} in the integrand, since they are not wholly independent. Hence, following the procedure adopted in the usual variation in Galilean coordinates, we must properly modify the integral by introducing equations of condition connecting these quantities, together with the corresponding undetermined Lagrangian multipliers. In the problem, we shall use

$$\frac{\partial G_{jk}}{\partial x_k} = -t_j, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

when expressed in general tensor form as our conditional equations. That is, we take

$$\mathrm{div}_k\, \mathbf{G}^{jk} = -t^j \quad \text{or} \quad \frac{\partial \mathbf{G}^{jk}}{\partial x_k} + \mathbf{G}^{lm}\mathrm{T}^j_{lm} = -\mathbf{T}^j,$$

where

$$\mathbf{T}^j = \sqrt{(-g)}\,.\,t^j,$$

and hence we get the generalized invariant action integral in its properly modified form as

$$\mathrm{I}'_G \equiv -\int\left\{\tfrac{1}{4}\mathbf{G}^{ik}G_{ik} - \phi_j'\left(\frac{\partial \mathbf{G}^{jk}}{\partial x_k} + \mathbf{G}^{lm}\mathrm{T}^j_{lm} + \mathbf{T}^j\right)\right\} dx,$$

the functions ϕ_j' being introduced in the usual way as auxiliary functions (the undetermined Lagrangian multipliers).

On the understanding that limit terms are to be everywhere omitted, and when the term $\delta\int \phi_n'\mathbf{T}^n\, dx$ is excluded, the variation of I'_G is equal to

$$-\int \delta\left[\tfrac{1}{4}\mathbf{G}^{ik}G_{ik} - \phi_i'\left(\frac{\partial \mathbf{G}^{ik}}{\partial x_k} + \mathbf{G}^{lm}\mathrm{T}^i_{lm}\right)\right] dx,$$

and this is equal to

$$\begin{aligned}-\int\Big[&\Big\{\tfrac{1}{2}\mathbf{G}^{ik} + \sqrt{(-g)}\left(\frac{\partial \phi_l'}{\partial x_m} - \phi_j'\mathrm{T}^j_{lm}\right)g^{lk}g^{mi}\Big\}\,\delta G_{ik}\\ &-\tfrac{1}{2}\mathbf{S}'_{ik}\,\delta g^{ik} - \phi_i' G^{lm}\mathrm{T}^i_{lm,j}\,\delta g^{ij}\\ &+\frac{\partial}{\partial x_j}\left\{\tfrac{1}{2}\phi_i'(\mathbf{G}^{lj}g^{im} + \mathbf{G}^{jm}g^{il} - \mathbf{G}^{lm}g^{ij})\right\}\delta g_{lm}\Big]\, dx,\end{aligned}$$

wherein

$$\mathbf{S}'_{ik} = \sqrt{(-g)}S'_{ik} = \sqrt{(-g)}\{G_{im}G_k^m - \tfrac{1}{4}G_{lm}G^{lm}g_{ik}\}.$$

We have, however, modified our action integral so that G_{ik} can be regarded as independent functions of the system and therefore the coefficients of the δG_{ik} can be equated to zero. In this way are derived the field equations

$$\tfrac{1}{2}G^{ik} + \sqrt{(-g)}\left\{\frac{\partial \phi_l'}{\partial x_m} - \phi_j' T^j_{lm}\right\} g^{lk}g^{mi} = 0,$$

or

$$G_{rs} = -\left(\frac{\partial \phi_r'}{\partial x_s} + \frac{\partial \phi_s'}{\partial x_r} - 2\phi_t' T^t_{rs}\right), \quad (G_{rs} = G_{sr}),$$
$$= -(\phi'_{r,s} + \phi'_{s,r}),$$

where, as usual in Riemannian geometry, $\phi'_{r,s}$ denotes the covariant derivative of ϕ_s'. In Galilean coordinates, since the g_{ij} have the constant values δ_i^j, the Christoffel symbols are zero and, consequently, the field equations assume the forms

$$G_{rs} = -\left(\frac{\partial \phi_r'}{\partial x} + \frac{\partial \phi_s'}{\partial x_r}\right)$$

obtained before in the special case.

11. The variation is now equal to

$$-\int\Big[\tfrac{1}{2}\mathbf{S}'^{ik}\delta g_{ik} - (\phi_i'\mathbf{G}^{lm}T_{lm,j})\,\delta g^{ij}$$
$$+ \frac{\partial}{\partial x_j}\{\tfrac{1}{2}\phi_i'(\mathbf{G}^{lj}g^{im} + \mathbf{G}^{im}g^{il} - \mathbf{G}^{lm}g^{ij})\}\,\delta g_{lm}\Big]\,dx.$$

We cannot, however, vary the g's absolutely independently, for they must be so restricted that the infinitesimal transformation of the coordinate system satisfies

$$\delta\sqrt{(g_{jk}\,dx_j\,dx_k)} = 0.$$

Hence, in the above, we insert

$$\delta g_{jk} = -\epsilon\left(\frac{\partial \xi^m}{\partial x_j}g_{mk} + \frac{\partial \xi^m}{\partial x_k}g_{jm} + \frac{\partial g_{jk}}{\partial x_m}\xi^m\right),$$

$$\delta g^{ik} = \epsilon\left(\frac{\partial \xi^k}{\partial x_m}g^{im} + \frac{\partial \xi^i}{\partial x_m}g^{mk} - \frac{\partial g^{ik}}{\partial x_m}\xi^m\right),$$

and then the variation is given by

$$-\epsilon\int\Big[-\tfrac{1}{2}\mathbf{S}'^{ik}\Big(2\frac{\partial\xi^m}{\partial x_i}g_{mk}+\frac{\partial g_{ik}}{\partial x_m}\xi^m\Big)$$

$$-(\phi_i'\mathbf{G}^{lm}\mathrm{T}_{lm,j})\Big(\frac{\partial\xi^i}{\partial x_k}g^{kj}+\frac{\partial\xi^j}{\partial x_k}g^{ik}-\frac{\partial g^{ij}}{\partial x_k}\xi^k\Big)$$

$$-\frac{\partial}{\partial x_j}\{\tfrac{1}{2}\phi_i'(\mathbf{G}^{lj}g^{im}+\mathbf{G}^{jm}g^{il}-\mathbf{G}^{lm}g^{ij})\}$$

$$\times\Big\{2\frac{\partial\xi^a}{\partial x_l}g_{am}+\frac{\partial g_{lm}}{\partial x_a}\xi^a\Big\}\Big]\,dx$$

$$=-\epsilon\int\xi^a\Big[\mathrm{div}_i\,\mathbf{S}_a'^i$$

$$+\frac{\partial}{\partial x_l}\Big\{g_{am}\frac{\partial}{\partial x_j}(\phi_i'\mathbf{G}^{lj}g^{im}+\phi_i'\mathbf{G}^{jm}g^{il}-\phi_i'\mathbf{G}^{lm}g^{ij})\Big\}$$

$$-\tfrac{1}{2}\frac{\partial g_{lm}}{\partial x_a}\Big\{\frac{\partial}{\partial x_j}(\phi_i'\mathbf{G}^{lj}g^{im}+\phi_i'\mathbf{G}^{jm}g^{il}-\phi_i'\mathbf{G}^{lm}g^{ij})\Big\}$$

$$+\frac{\partial}{\partial x_k}\{\phi_a'\mathbf{G}^{lm}\mathrm{T}^k{}_{lm}+\phi_i'\mathbf{G}^{lm}\mathrm{T}_{lm,a}g^{ik}\}$$

$$+\frac{\partial g^{ij}}{\partial x_a}\{\phi_i'\mathbf{G}^{lm}\mathrm{T}_{lm,j}\}\Big]\,dx,$$

The ξ's being now independent we can equate their coefficients to zero and thus derive four equations, which, assuming the forms

$$\mathrm{G}_{rs}=-(\phi'_{r,s}+\phi'_{s,r}),$$

can be shown to reduce to the identities

$$\mathrm{div}_i\,\mathbf{S}'^i{}_m=\frac{\partial}{\partial x_i}(\mathbf{G}^{ik}\mathrm{G}_{mk})-\tfrac{1}{2}\mathbf{G}^{ik}\frac{\partial\mathrm{G}_{ik}}{\partial x_m},$$

which are equivalent, in Galilean coordinates, to the equations satisfied by the stress energy tensor in paragraph 6 above, viz.,

$$\frac{\partial\mathrm{T}_{mi}}{\partial x_i}=t_k\mathrm{F}'_{mk}=\mathrm{F}_m',$$

where

$$\mathrm{T}_{mi}=\mathrm{G}_{mr}\mathrm{G}_{ri}-\tfrac{1}{4}\mathrm{G}_{pq}\mathrm{G}_{pq}\delta_{mi}+\mathrm{G}_{ik}\frac{\partial\phi_m'}{\partial x_k}-t_i\phi_m'$$

$$=-\Big(\tfrac{1}{4}\mathrm{G}_{pq}\mathrm{G}_{pq}\delta_{mi}+\mathrm{G}_{ik}\frac{\partial\phi'_k}{\partial x_m}+t_i\phi'_m\Big).$$

12. For the rest of the variation, we have

$$\int \phi_j' \delta \mathbf{T}^j \, dx,$$

and in terms of ξ^a this is equal to

$$\epsilon \int \xi^a \left\{ \mathbf{T}^m \left(\frac{\partial \phi_m'}{\partial x_a} - \frac{\partial \phi_a'}{\partial x_m} \right) \right\} dx,$$

where we have supposed that t_m is subject to the continuity condition $\partial t_m / \partial x_m = 0$, which in general tensor form is

$$\frac{\partial \mathbf{T}^m}{\partial x_m} = 0.$$

This last result can be used for determining the force acting per unit volume on the charges in the field. For this purpose, however, an arbitrary virtual displacement $\delta_0 x_k$ (defined by variations of the coordinates of the charges) for the volume element must be considered as distinct from a mere transformation of the coordinate system of the type introduced in the foregoing discussion. Also, we must include in our Lagrangian function an intrinsic term which is entirely dependent upon the mass particles within the element. But if F_j' is the gravitational force acting during the displacement on the particles inside the small volume, then we have work done of amount

$$(\mathrm{F}_j' \delta_0 x_j),$$

and therefore we shall choose the intrinsic term in our invariant action integral so that its variation is given by

$$\int -\sqrt{(-g)} \cdot \mathrm{F}_j' \, \delta_0 x_j \, dx.$$

Besides this term, we have also to consider the variation of

$$\mathrm{I}_{\mathrm{G}}' = -\int \left\{ \tfrac{1}{4} \mathbf{G}^{ik} \mathrm{G}_{ik} - \phi_j' \left(\frac{\partial \mathbf{G}^{jk}}{\partial x_k} + \mathbf{G}^{lm} \Gamma^j_{lm} + \mathbf{T}^j \right) \right\} dx.$$

Only the last term of I_{G}', however, makes any contribution to the present variation, and this is equal to

$$\int \left(\frac{\partial \phi_k'}{\partial x_j} - \frac{\partial \phi_j'}{\partial x_k} \right) \mathbf{T}^k \, \delta x_j \, dx,$$

since $\epsilon \xi^j$ in the above is now replaced by $\delta_0 x_j$. Hence, for the complete variation, we have

$$\int \left\{ -\sqrt{(-g)} \mathrm{F}_j' + \left(\frac{\partial \phi_k'}{\partial x_j} - \frac{\partial \phi_j'}{\partial x_k} \right) \mathbf{T}^k \right\} \delta_0 x_j \, dx,$$

and since the $\delta_0 x_j$ are arbitrary and independent of one another and of all variations, we thus obtain the set of equations,

$$F_j' = \left(\frac{\partial \phi_k'}{\partial x_j} - \frac{\partial \phi_j'}{\partial x_k}\right) t^k = F'_{jk} t^k,$$

which, in Galilean coordinates, reduce to

$$F_j' = \left(\frac{\partial \phi_k'}{\partial x_j} - \frac{\partial \phi_j'}{\partial x_k}\right) t_k,$$

which is the last of the results which constitute the general formulation of the theory.

With this, then, we conclude the present note, leaving the analysis of the theory as regards its application to special problems, for future consideration.

Lastly, it is a pleasure here to acknowledge our indebtedness to Professor G. H. Livens for much assistance and helpful advice throughout the course of the work, and to the Council of the University of Wales for studentship grants which made possible the undertaking of the work.

V. *The Clock Problem in Relativity.*

By J. W. Campbell, *Ph.D.**

BY the clock problem in relativity is meant the problem of the relative flows of time indicated by two clocks which do not remain relatively at rest. Of particular interest is the case where two clocks, originally together and at rest, separate and meet again. This latter problem was discussed by Einstein in a paper † in which he considered several of the puzzling aspects of relativity. He gave general principles for the solution of the problem and expressed them in terms of the following specially simple case: One clock remains at rest in a Galilean frame of reference while another moves off from it along a straight line and returns by the same path. The second clock attains its velocity quickly at the beginning, and the reversing also is of an impulsive character, so that most of the relative motion takes place at uniform speed. The details of how the solution

* Communicated by the Author.

† A. Einstein, "Dialog über Einwände gegen die Relativitatstheorie," *Die Naturwissenschaften*, vi. p. 697 *et seq.* (1918).

works out in this case are given by Kopff*. It is the purpose of this note to show how the principles can be applied when the second clock describes a closed path of any kind and in any manner.

Suppose that a clock A is at rest in a frame of reference which is Galilean or inertial in the following sense:

(1) A is not in the vicinity of ponderable matter.

(2) All particles observed from A and not in the neighbourhood of other matter follow straight line paths (*i. e.*, paths given by a linear law) in the frame of reference chosen, and this regardless of their distance from A.

Suppose that a clock B has, as observed from A, an acceleration $(\ddot{x}, \ddot{y}, \ddot{z})$ which is given by equations of the form

$$\ddot{x} = \ddot{x}_1 + \frac{\partial U}{\partial x}, \quad \ddot{y} = \ddot{y}_1 + \frac{\partial U}{\partial y}, \quad \ddot{z} = \ddot{z}_1 + \frac{\partial U}{\partial z},$$

where U is a potential function arising from the gravitational field of matter in the vicinity of B and $(\ddot{x}_1, \ddot{y}_1, \ddot{z}_1)$ is the part of B's acceleration which is due to any other causes.

Then if $v^2 = \dot{x}^2 + \dot{y}^2 + \dot{z}^2$ and c is the velocity of light, the lag of the clock B due to velocity alone in an interval t_1 to t_2 as observed by A is

$$\int_t^{t_2} \frac{v^2}{2c^2} dt,$$

and due to the potential difference of the positions of A and B the lag in the same interval is

$$\int_{t_1}^{t_2} \frac{U}{c^2} dt.$$

Thus the total lag of B as observed by A is

$$\int_{t_1}^{t_2} \left(\frac{v^2}{2c^2} + \frac{U}{c^2} \right) dt.$$

To see the matter from the standpoint of a reference system in which B is at rest, a homogeneous gravitational field of acceleration $(-\ddot{x}, -\ddot{y}, -\ddot{z})$ is imposed everywhere, where A is at $(-x, -y, -z)$, while the "force" originally acting on B continues to act.

A. Kopff, 'The Mathematical Theory of Relativity,' p. 124 *et seq.*

The excess of the imposed potential at A over that imposed at B is $x\ddot{x}+y\ddot{y}+z\ddot{z}$, as is readily seen by integrating the potential gradient from B to the equipotential plane through $(-x, -y, -z)$, and so the resulting excess of potential at A over that at B is

$$-U+x\ddot{x}+y\ddot{y}+z\ddot{z}.$$

The gain of the clock at A, as seen by B, due to this potential difference is

$$\begin{aligned}
&-\frac{1}{c^2}\int_{t_1}^{t_2}(-U+x\ddot{x}+y\ddot{y}+z\ddot{z})\,dt \\
&\quad=\int_{t_1}^{t_2}\frac{U}{c^2}\,dt-\frac{1}{c^2}\int_{t_1}^{t_2}(x\,d\dot{x}+y\,d\dot{y}+z\,d\dot{z}) \\
&\quad=\int_{t_1}^{t_2}\frac{U}{c^2}\,dt-\frac{1}{c^2}\Big(x\dot{x}+y\dot{y}+z\dot{z}\Big)_{t_1}^{t_2} \\
&\qquad\qquad+\frac{1}{c^2}\int_{t_1}^{t_2}(\dot{x}\,dx+\dot{y}\,dy+\dot{z}\,dz) \\
&\quad=\int_{t_1}^{t_2}\frac{U}{c^2}\,dt-\frac{1}{c^2}\Big(x\dot{x}+y\dot{y}+z\dot{z}\Big)_{t_1}^{t_2} \\
&\qquad\qquad+\frac{1}{c^2}\int_{t_1}^{t_2}(\dot{x}^2+\dot{y}^2+\dot{z}^2)\,dt \\
&\quad=\int_{t_1}^{t_2}\frac{U}{c^2}\,dt-\frac{1}{c^2}\Big(x\dot{x}+y\dot{y}+z\dot{z}\Big)_{t_1}^{t_2}+\int_{t_1}^{t_2}\frac{v^2}{c^2}\,dt.
\end{aligned}$$

The loss of the clock at A due to velocity alone is

$$\int_{t_1}^{t_2}\frac{v^2}{2c^2}\,dt.$$

Hence the net gain of the clock at A as seen by B is

$$\int_{t_1}^{t_2}\Big(\frac{v^2}{2c^2}+\frac{U}{c^2}\Big)\,dt-\frac{1}{c^2}\Big(x\dot{x}+y\dot{y}+z\dot{z}\Big)_{t_1}^{t_2}.$$

Therefore the loss of B as seen by A and the gain of A as seen by B agree provided the term

$$\frac{1}{c^2}\Big(x\dot{x}+y\dot{y}+z\dot{z}\Big)_{t_1}^{t_2}$$

vanishes, and this will be true provided that at t_1 and t_2 the positions (x, y, z) and the velocities $(\dot{x}, \dot{y}, \dot{z})$ of B are the same.

Hence *if B moves in a Galilean frame of reference over a closed path of any kind and in any manner, then between any two passages of the same point with the same velocity the gains as seen by B of all clocks at rest in the Galilean frame and not in the vicinity of ponderable matter are the same, and they are precisely equal to the loss of the clock B as seen from any point in the Galilean frame which is not in the vicinity of ponderable matter.*

Two special cases may be noted.

1. If A and B are together, except for separation during the interval t_1 to t_2, then the velocity of B at both t_1 and t_2 is zero and so the expression $\left(x\dot{x}+y\dot{y}+z\dot{z}\right)_{t_1}^{t_2}$ vanishes.

Hence if A remains at rest in a Galilean frame as already explained, and if B makes an excursion over a path of any kind and in any manner, the loss of B as seen from A will be equal to the gain of A as seen from B.

This is a generalization of the case treated by Kopff.

2. If the acceleration of B is due to a gravitational field only and if the "centre of attraction" for B is at rest relative to A, then B describes a closed orbit as seen by A and passes through a given point with the same velocity each time. Therefore, here again, if the interval t_1 to t_2 is any multiple of the period of B the gain of the clock A as seen from B is equal to the loss of the clock B as seen from A.

University of Alberta.
September, 1932.

VI. *The Raman Effect in Organic Sulphides and some Thio-Compounds.* *By* V. N. Thatte, *Assistant Professor of Physics and* A. S. Ganesan, *M.A., Ph.D. (London)**.

[Plate IV.]

IN a preliminary note published by us in 'Nature' † we described some of the characteristic frequencies in the Raman Spectra of ethyl and allyl sulphides. In this paper is reported a more detailed account of the study of scatttering in a number of organic sulphides and sulphur compounds. These investigations were carried out early

* Communicated by the Authors.
† Thatte and Ganesan, 'Nature,' cxxvii. p. 306 (1931).

last year, but pressure of work delayed their publication. The substances studied were ethyl, propyl, allyl, isobutyl and benzyl sulphides, iso-amyl hydrosulphide, thio-

TABLE I.

Ethyl sulphide.

Modified lines. Wave-length in air.	Modified lines. Intensity.	Wave-number in vacuum cm.$^{-1}$.	Exciting line. of mercury arc.	Wave-number difference $\Delta\nu$.
5006·0	2	19970	4358·3 (22938)	2968
4995·5	5	20012	„	2926
4990·5	0	20032	„	2906
4980·6	1	20072	„	2866
4653·7	3	21482	„	1456
4633·1	2	21578	4077·8 (24510)	2932
4601·0	4	21728	4046·6 (24705)	2977
4591·6	10	21773	„	2932
4588·5	2	21787	„	2918
4579·1	3	21832	„	2873
4567·3	1	21889	4358·3	1049
4551·4	2	21965	„	973
4515·9	0	22138	„	800
4508·6	0	22173	„	765
4494·8	3	22241	„	697
4484·2	4	22294	„	644
4419·6	1	22620	„	318
4299·4	3	23252	4046·6	1453
4261·3	1*d*	23460	„	1245
4227·1	2	23650	„	1055
4212·3	2	23733	„	972
4180·4	0*d*	23914	„	791
4163·8	3	24009	„	696
4156·3	4	24053	„	652
4094·8	4	24414	3654·8 (27354)	2940
4087·4	4	24458	3650·1 (27389)	2931

$\Delta\nu$ ..	318	648	696	787	972	1052	1245	1454	2870	2912	2932	2970
$\lambda(\mu)$ ..	31·4	15·4	14·4	12·7	10·3	9·51	8·03	6·88	3·48	3·43	3·41	3·37

glycollic acid and thiacetic acid. Some of these liquids have been recently studied by Venkateswaran * and his results are in good agreement with our analysis

* Venkateswaran, Ind. Journ. Phys. vi. p. 51 (1931).

of the spectra. The substances were obtained from Kahlbaum and further purified and made dust free by

TABLE II.

Propyl Sulphide.

Modified lines. Wave-length in air.	Modified lines. Intensity.	Wave-number in vacuum cm.$^{-1}$.	Exciting line of mercury arc.	Wave-number difference $\Delta\nu$.
5005·2	3	19974	4358·3 (22938)	2964
4996·5	3	20008	,,	2930
4990·4	2	20033	,,	2905
4977·0	2	20087	,,	2851
4652·3	2	21489	,,	1449
4621·5	1	21632	,,	1306
4599·6	6	21735	4046·6 (24705)	2970
4588·7	6	21786	,,	2919
4584·2	4	21807	,,	2902
4577·5	6	21840	,,	2865
4564·1	2	21904	4358·3	1034
4551·5	0	21964	4347·5 (22995)	1031
4535·5	1	22042	4358·3	896
4515·0	0	22142	,,	796
4500·5	2	22213	,,	725
4486·2	2	22285	,,	653
4431·3	1	22560	,,	378
4414·2	2	22648	,,	290
4297·5	2*d*	23263	4046·6	1442
4268·3	1	23422	,,	1283
4235·3	1	23604	,,	1101
4223·5	2	23670	,,	1035
4198·5	1	23811	,,	894
4190·1	0	23859	,,	846
4170·5	2	23971	,,	734
4157·5	2*d*	24046	,,	659
4100·6	2	24380	3663·3 (27290)	2910
4090·0	2	24443	3654·8 (27354)	2911
4083·8	4	24480	3650·1 (27389)	2909

$\Delta\nu$ ...	290	378	656	730	796	846	895	1033	1100	1294
			1445	2858	2900	2920	2965			
$\lambda(\mu)$ ..	34·5	26·5	15·2	13·7	12·6	11·8	11·2	9·68	9·09	7·73
			6·92	3·50	3·45	3·42	3·37			

distillation in vacuum. They were contained in Wood's tubes and the mercury arc was used as the source of

illumination. The photographs were taken with the E 3 quartz spectrograph of Adam Hilger on high speed golden iso-zenith plates. Exposures varying from 10 to 20 hours were given using, in some cases, suitable liquid and colour filters to cut out the unwanted radiations from the light of the mercury arc. The scattered spectrum of benzyl sulphide which is a solid at the room tem-

TABLE III.

Iso-butyl Sulphide.

Modified lines.		Wave-number in vacuum cm.$^{-1}$.	Exciting line of mercury arc.	Wave-number difference $\Delta\nu$.
Wave-length in air.	Intensity.			
5003·7	3	19980	4358·3 (22938)	2958
4984·3	3*d*	20057	„	2881
4654·1	2	21480	„	1458
4624·8	2*d*	21616	„	1322
4598·6	5	21740	4046·6 (24705)	2965
4578·4	5	21835	„	2870
4546·4	2	21989	4358·3	949
4518·4	2	22125	„	813
4502·3	2	22204	„	734
4462·5	0	22402	„	536
4441·6	1	22508	„	430
4426·4	0	22585	„	353
4300·4	2	23247	4046·6	1458
4276·6	1	23377	„	1328
4257·7	0	23480	„	1225
4227·1	0	23650	„	1055
4208·7	2*d*	23754	„	951
4184·9	2	23889	„	816
4169·7	2*d*	23976	„	729
4093·2	3	24424	3650·1 (27389)	2965

$\Delta\nu$ ...	353	430	536	731	814	950	1055	1225	1325	1458	2875	2962
$\lambda(\mu)$ ..	28·3	23·3	18·7	13·7	12·3	10·5	9·51	8·16	7·55	6·86	3·48	3·38

perature was taken in a solution of carbon tetrachloride whose Raman spectrum is well known. The thio-acids as received from Kahlbaum were coloured and they were distilled a number of times, first in air and then in vacuum till they became clear and free from sulphur suspensions.

The results are tabulated in Tables I. to VIII. The first column gives the wave-lengths in air expressed

in international angstroms and they are correct to about ·4 of an angstrom. The second column gives the intensity of the lines visually estimated denoting the

TABLE IV.

Allyl Sulphide.

Modified lines. Wave-length in air.	Intensity.	Wave-number in vacuum cm.$^{-1}$.	Exciting line of mercury arc.	Wave-number difference $\Delta\nu$.
5034·2	1	19859	4358·3 (22938)	3079
5014·0	2	19939	,,	2999
4991·0	3	20030	,,	2908
4693·7	6	21299	,,	1639
4662·2	0	21443	,,	1495
4644·5	4*d*	21525	,,	1413
4621·6	4*d*	21631	4046·6 (24705)	3074
4607·8	5	21696	,,	3009
4601·3	3	21727	,,	2978
4587·8	5	21791	,,	2914
4574·1	1	21856	4358·3	1082
4557·7	1	21935	,,	1003
4542·8	2	22006	,,	932
4504·8	4*d*	22192	,,	746
4473·6	3	22347	,,	591
4455·5	1	22438	,,	500
4438·9	3	22522	,,	416
4423·2	1	22602	,,	336
4405·2	0	22694	,,	244
4334·1	3	23066	4046·6	1639
4291·3	5*d*	23296	,,	1409
4270·6	5	23409	,,	1296
4254·5	4*d*	23498	,,	1207
4217·8	2	23702	,,	1003
4204·7	3	23776	,,	929
4173·5	5*d*	23954	,,	751
4145·3	4	24117	,,	588
4130·3	3	24204	,,	501
4115·9	4*d*	24289	,,	416
4112·9	2	24307	3650·1 (27389)	3082
4101·1	4	24377	,,	3012
4090·5	4	24439	3654·8 (27354)	2915
4085·2	4	24471	3650·1	2918

$\Delta\nu$ ... 240 **332** 416 500 590 748 930 1003 1082 1206
1302 1410 1495 1639 2910 3005 3075

$\lambda(\mu)$ .. 41·7 30·1 24·0 20·0 16·9 13·4 10·8 9·97 9·24 8·29
7·68 7·09 6·69 6·10 3·44 3·33 3·25

most intense line by 10 and the line that is but just visible on the plate as 0. The letter *d* after the intensity shows that the line is diffuse and probably consists of two or more lines not resolved. In the third column are entered the wave-numbers corrected to vacuum and in the fourth column the incident exciting lines of the mercury arc. The last column gives the frequency shifts in wave-numbers per cm. At the foot of each

TABLE V.

Benzyl Sulphide in Carbon tetra-chloride.

Modified lines.		Wave-number in vacuum cm.$^{-1}$.	Exciting line of mercury arc.	Wave-number difference $\Delta\nu$.
Wave-length in air.	Intensity.			
5028·6	1	19881	4358·3	3057
			(22938)	
4687·1	2	21329	,,	1609
4618·0	0	21648	4046·6	3057
			(24705)	
4610·0	1	21686	4358·3	1252
4559·2	2	21927	,,	1011
4511·4	2*d*	22160	,,	[778]
4493·0	1	22250	,,	688
4447·9	10	22476	,,	[462]
4419·3	5	22621	,,	[317]
4401·1	4	22715	,,	[223]
4316·5	3*dv*	23160	,,	[−222]
4300·2	3	23248	,,	[−310]
4273·2	2	23395	,,	[−457]

$\Delta\nu$ ...	688	1011	1252	1609	3057
$\lambda(\mu)$ ..	14·5	9·89	7·99	6·22	3·27

table are given the Raman shifts together with their reciprocals giving the infra-red frequencies expressed in μ. The infra-red absorption spectra of these liquids have been studied by F. K. Bell * and the values obtained from his absorption curves are referred to in the discussion of the results in the case of each liquid.

Ethyl Sulphide.—The spectrum of ethyl sulphide is comparatively very simple and consists of a few prominent Raman shifts. These can be divided into

* Bell, Berichte der Deutschen Chem. Gesellschaft, lx. p. 1749 (1927) and lxi. p. 1918 (1928).

two groups, one arising from the C–H oscillations and the other whose origin is in the linking of the sulphur

TABLE VI.

Iso-amyl hydrosulphide.

Modified lines. Wave-length in air.	Modified lines. Intensity.	Wave-number in vacuum cm.$^{-1}$.	Exciting line of mercury arc.	Wave-number difference $\Delta\nu$.
5006·4	4	19969	4358·3	2969
			(22938)	
4990·4	4	20033	,,	2905
4981·6	4	20068	,,	2870
4652·4	4*d*	21488	,,	1450
4638·4	3	21553	,,	1385
4630·3	3	21591	,,	1347
4620·3	2	21638	,,	1300
4598·0	8	21742	4046·6	2963
			(24705)	
4590·9	8	21776	,,	2929
4578·9	8	21833	,,	2872
4555·6	1	21945	4077·8	2565
			(24510)	
4517·7	5	22129	4046·6	2576
4503·9	2	22197	4358·3	741
4488·2	4	22275	,,	663
4440·7	1	22513	,,	425
4413·7	2	22651	,,	287
4299·1	2*d*	23254	4046·6	1451
4279·9	1*d*	23358	,,	1347
4270·5	0	23410	,,	1295
4257·8	0	23480	,,	1225
4252·0	0	23512	,,	1193
4237·7	2	23591	4358·3	−653
4184·5	2	23891	4046·6	814
4171·1	2*d*	23968	,,	737
4158·4	3	24041	,,	664
4092·9	4*d*	24425	3650·1	2964
			(27389)	
4086·0	4*d*	24467	,,	2922
4028·1	3	24818	,,	2571
4002·8	1	24975	4046·6	−270

$\Delta\nu$ ..	280	425	663	740	810	1194	1225	1298	1347	1450
			2570	2870	2920	2965				
$\lambda(\mu)$..	35·7	23·5	15·1	13·5	12·3	8·38	8·16	7·70	7·42	6·90
			3·89	3·48	3·42	3·37				

to the carbon atoms. To the first group belong the shifts 1454, 2870, 2932 and 2970 which have identical values in alcohols and all aliphatic compounds. To the

second group belong the pair of strong and sharp shifts 648, 698, the double shifts 972 and 1052, and the two weak and diffuse shifts 318 and 1245 respectively. A comparison of the scattered spectrum of ethyl sulphide with that of ethyl ether shows the effect of substituting the oxygen atom by the sulphur atom. This substitution does not affect the longer shifts that are attributed to C–H, but modifies to a marked extent the shorter shifts connected with the C.S.C. group. Corresponding to 972 and 1052 of the sulphide we have

TABLE VII.

Thiacetic acid.

Modified lines. Wave-length in air.	Intensity.	Wave-number in vacuum cm.$^{-1}$.	Exciting line of mercury arc.	Wave-number difference $\Delta\nu$.
4995·6	3	20012	4358·3 (22938)	2926
4706·2	4	21243	,,	1695
4647·2	1*d*	21512	,,	1426
4586·8	1	21796	4046·6 (24705)	2909
4558·6	2*d*	21931	4358·3	1007
4524·4	2	22097	,,	841
4483·2	5	22300	,,	638
4468·1	1	22375	,,	563
4447·4	3	22479	,,	459

$\Delta\nu$ ..	459	563	638	841	1007	1426	1695	2920
$\lambda(\mu)$	21·8	17·8	15·7	11·9	9·93	7·01	5·90	3·42

$\Delta\nu$. Acetic acid. 283, 362, 446 (623), 766 (901), 1280, 1364 (1433), 1670 (2944).

the ether shifts 928 and 1027 ; while instead of the strong pair 648 and 696 of C.S.C. oscillation, we have two equally strong shifts 441 and 845 due to C.O.C. in diethyl ether.

Propyl Sulphide.—The spectrum of this liquid is similar to that of ethyl sulphide but contains a greater number of lines. Corresponding lines assume a more complicated structure and the C–H shifts are the most conspicuous. The C.S.C. frequencies assume the double values 290, 378 ; 656, 730 ; and 895, 1033 ; all these

doublets being more or less equally strong. The infra-red absorption spectrum of this liquid has been studied by Bell (*loc. cit.*) from whose curve the following absorption wave-lengths expressed in μ are taken :—2·2 (3·3), (6·8), 7·2 (7·7), (8·0), 9·1, 9·5 (11·2) and 11·8 μ. The figures in brackets show strong absorption frequencies. There is a general agreement between the infra-red

TABLE VIII.

Thio-glycollic acid.

Modified lines. Wave-length in air.	Modified lines. Intensity.	Wave-number in vacuum cm.$^{-1}$.	Exciting line of mercury arc.	Wave-number difference $\Delta\nu$.
4997·9	1	20003	4358·3	2935
			(22938)	
4708·6	1*d*	21231	,,	1707
4677·1	1*d*	21375	,,	1563
4643·5	2*d*	21529	,,	1409
4594·7	3*d*	21758	4046·6	2947
			(24705)	
4558·2	2	21932	4358·3	1006
4540·0	2	22020	,,	918
4518·7	4	22124	,,	814
4494·7	0	22242	,,	696
4473·1	1*d*	22349	,,	589
4442·2	1*d*	22505	,,	433
4217·5	0	23704	4046·6	1001
4201·1	0	23796	,,	909
4185·8	2*d*	23883	,,	822
4160·5	1	24029	,,	676
4142·2	1	24135	,,	570
4132·0	1	24194	,,	511
4090·8	1*d*	24438	3650·1	2951
			(27389)	

$\Delta\nu$ ...	433	511	580	686	818	914	1004	1409	1563	1707	2950
$\lambda(\mu)$ ..	23·1	19·6	17·2	14·6	12·2	10·9	9·96	7·10	6·40	5·86	3·39

absorption values and the Raman shifts observed, though the strong absorption at 8·0 μ is not represented in the scattered spectrum.

Iso-butyl sulphide.—The three strong lines in this spectrum correspond to $\Delta\nu$ 731, 814 and 950. The C–H shifts at 3·4 μ instead of being diffuse and possessing a structure is quite sharp and has the value 2962. We shall return subsequently to the behaviour of this band

in the several compounds studied. The new shift $\Delta\nu 1325$ which is not present in the normal sulphides is probably due to the isomeric form of the compound. The infra-red absorption frequencies of normal butyl sulphide are 2·2, 3·3, 6·9, 7·2, 7·8, 9·0, 10, 10·5 and 10·8 μ.

Allyl Sulphide.—The Raman spectrum of allyl sulphide is very different from the spectra of the other sulphides both in the richness of the lines and in their intensity and it bears the same contrast to the other spectra as the spectrum of allyl alcohol bears to the spectra of the normal alcohols. There is a marked tendency for the Raman lines in this spectrum to group themselves into doublets of constant frequency intervals and this feature is also seen in the spectrum of allyl alcohol *. Thus the pairs of lines (240, 416), (332, 500), (416, 590) and (748, 930) have a constant separation of about 175 wave-numbers. Similarly the pairs of lines (1003, 1206), (1002, 1302) and (1410, 1639) have an interval of about 215 wave-numbers. The aliphatic C–H shifts are very strong but displaced towards the longer wave-length side as in allyl alcohol. The characteristic shifts of C.S.C. take the values 416, 590 and 748 respectively. 1206 and 1302 that are weak in the other sulphides are quite strong in this spectrum. One of the prominent lines is what corresponds to 1639 which is absent in all the other spectra. These features are evidently due to the unsaturated nature of the compound and are to be observed in the spectra of the other allyl compounds. In this connexion it may not be out of place to compare this spectrum with that of the other allyl sulphur compound which we had studied †, viz. allyl isothiocyanate. The Raman shifts 416, 590, 748 and 930 of allyl sulphide correspond to the shifts 398, 561, 710 and 916 respectively of isothiocyanate, and the former are consistently higher than the latter. But in the region of the longer shifts the isothiocyanate shifts are higher than the sulphide shifts; thus we have 1254, 1340, 1431 and 1650 of isothiocyanate corresponding to 1207, 1302, 1410 and 1639 of the sulphide. In isothiocyanate the C–H frequencies have the values 1431, 2846 and 2920, while

* Ganesan and Venkateswaran, Ind. Journ. Phys. v. p. 209 (1929).
† Ganesan and Thatte, Phil. Mag. xii. p. 827 (1931).

in the sulphide spectrum they correspond to 1495, 2910, 3005 and 3075.

Benzyl Sulphide.—As mentioned previously the spectrum of this substance was taken in a solution of carbon tetrachloride, and the results are set forth in Table V. The numbers in square brackets in the last column give the CCl_4 frequencies. These came out quite sharp and without any apparent change in their position. The lines due to benzyl sulphide were a little diffuse. Five frequencies had come out of which 1011, 1609 and 3057 were strong and 1252 and 688 were faint. The first two are the frequencies characteristic of the benzene ring and whose values in benzene are 991 and 1592. It is well-known that these frequencies have increased values in substituted compounds. The third frequency 3057 is the aromatic C–H shift. The last two frequencies are due to the C.S.C. group. The strong infra-red absorptions in this liquid are 3·3, 6·3, 6·7, 6·9, 8·0, and 9·3 μ.

Iso-Amylhydro-sulphide.—This is a spectrum rich in lines. A very characteristic frequency 2570 which does not appear in any of the other sulphides is present here and is evidently due to the S–H bond. Ellis * has studied the infra-red absorption of a number of hydrosulphides and he finds two frequencies corresponding to 3·80 μ and 1·99 μ, one of which is the first overtone of the other. The Raman shift gives a slightly higher value 3·89 μ. The C.S.C. frequencies 280, 663, 740 and 810 are very prominent. The chief infra-red frequencies obtained by Bell (*loc. cit.*) are 3·3, 3·8, 6·8, 7·2, 7·7, 8·0, 8·5, 8·9, and 10·2 μ.

Thio-glycollic acid.—The liquid was viscous and the scattered spectrum showed a strong and continuous background and in this respect may be compared to glycerine and glycol. The strongest lines were the ones corresponding to $\Delta\nu$ 814 and 1409, the corresponding shifts in glycol † being 871 and 1463.

Thiacetic acid.—The liquid as received was deeply coloured and even after a number of distillations, first

* Ellis, J. A. C. S. l. p. 2113 (1928).
† Thatte and Shahane, Ind. Journ. Phys. vi. p. 155 (1931).

in air and then *in vacuo* was slightly yellowish. The spectrum consequently showed a dark and continuous background. The strongest line corresponds to $\Delta\nu 638$ and the other prominent shifts are 459, 841 and 1695. A comparison of these frequencies with those of acetic acid shows that there is a general change in their values and also in their intensities. The strongest line corresponding to $\Delta\nu 901$ in acetic acid has no corresponding frequency in thiacetic acid.

General Discussion of the Results.

The investigation of the scattered spectra in this series of organic sulphides throws some light on the probable origins of some of the characteristic frequencies of the molecules and also helps us to understand how these frequencies are affected by the presence of other atoms or groups of atoms in the molecule. From a study of the tables it is evident that the three frequencies at 1450, 2870 and 2930 are common to all the substances studied, and it is well-known that these are due to the oscillations of the C–H bond in the molecule. It is interesting to study how these frequencies vary as we go from one compound to another. Taking the last one first, we find that in ethyl sulphide the 3·4 μ absorption is a broad band extending over about 15 angstroms or 60 wave-numbers and consists of three components, a faint but sharp one at 2912 and a pair of diffuse and bright lines at 2932 and 2970. In propyl sulphide there seems to be a general shift towards the shorter wave-length side, the three values being 2900, 2920 and 2965 respectively. In isobutyl sulphide the band has become quite narrow and the mean value of the shift is 2962. In this connexion we may mention that in isobutyl alcohol also this shift has a single value of 2965 unlike as in the other alcohols where a definite structure is exhibited. In allyl sulphide the outer components are shifted considerably towards the red side and have the values 3005 and 3075. This is also to be noticed in allyl alcohol where the values are 3014 and 3079 respectively. In benzyl sulphide the C–H oscillation takes the value 3079 in agreement with its value in benzene and all benzene compounds. In the two thio-acids the structure of this band could not be

advantageously studied owing to the presence of the continuous background.

The absorption at 3·48 μ or $\Delta\nu$ 2870 occupies almost identical positions in all the sulphides except in benzyl sulphide where it is absent, and in allyl sulphide where it is replaced by the shift at $\Delta\nu$ 2910, which is almost as strong as the other two components. The behaviour of the shift $\Delta\nu$ 1450 (6·9 μ) goes *pari passu* with that of the shifts $\Delta\nu$ 2920 (3·4 μ). We may mention that the one is about half the value of the other. In propyl sulphide its value is 1445 corresponding to 2920. In ethyl sulphide it increases to 1454 as the second shift increases to 2930. A further increase is shown in isobutyl sulphide where the two values are 1458 and 2962 respectively. Again in allyl sulphide it has a high value 1495 corresponding to the equally high value 3075 in the other shift.

The other common frequencies in the sulphides are those to be attributed to the C.S.C group. In the spectrum of methyl sulphide, which has been studied by Venkateswaran (*loc. cit.*), in addition to the C–H frequencies four new shifts 284 (691, 743) and 1335 are obtained whose origins are to be found in the oscillations of the C.S.C group. To explain these frequencies on the basis of dynamical considerations the author assumes the molecule to be of the type AX_2, A, representing the sulphur atom and X the alkyl group. Such a configuration will give rise to three frequencies corresponding to the three natural possible modes of vibration of which the symmetric type of vibration gives rise to the strongest shift which is double, viz. 691 and 743. If these frequencies are due to the C.S.C group, then it will be natural to expect that their values will vary from compound to compound depending upon how the two carbon atoms are linked to the other atoms in the molecule. A glance at the table shows that not only do the values change but the lines also seem to take a structure, each line in turn splitting up into further components. In propyl sulphide the single frequency 318 of ethyl sulphide becomes split up into two shifts 290 and 378 and in allyl sulphide into the three components 240, 332, and 416. The strong shifts 691, 743, of methyl sulphide due to the symmetric mode of oscillation of C.S.C, have the values

648, 696 in ethyl sulphide ; 656, 730 in propyl sulphide and 590, 748 in allyl sulphide. In benzyl sulphide this appears as a single line at 688. These two shifts are comparable with the shifts 655 and 800 of carbon disulphide due to the oscillations of S.C.S.

The authors desire to express their thanks to Professor M. Owen for his kind interest in the work.

College of Science,
Nagpur, India.
April 1932.

VII. *On Rayleigh's Principle.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

In his recent paper in the Supplementary (November) number of the Philosophical Magazine Mr. Cornock has referred to my own researches in connexion with Rayleigh's Principle. I should like to add two supplementary notes to his paper.

In the first place it is necessary to emphasize the fact that although the theory of my method was developed by means of Green's Functions, yet the practical method of successive approximation which I advocated is entirely independent of the construction or use of these functions. Actually the method sketched on p. 277 of my first paper (Lond. Math. Soc. Proc. Ser. 2, vol. xxix.), is identical with that devised by Picard and employed by Cornock.

The second point to which I desire to draw attention is that the most effective use which can be made of the approximating functions is by means of Rayleigh's Principle. The method used by Cornock seems to be similar to that employed by J. Morrow some years ago, and the results obtained by this method are well known to be far from close approximations to the accurate value required.

I have shown in the two papers quoted by Cornock that Rayleigh's Principle applied to the first two or three members of a sequence of approximating functions

will give the critical parameters required with close and known degrees of accuracy. May I also add that, in conjunction with Dr. W. G. Bickley, of the City and Guilds (Engineering) College, I have written a much fuller account of the theory and practice of Rayleigh's method as applied to problems of engineering in a book to be published shortly by the Oxford University Press. This will give abundant illustrations of the application of Rayleigh's Principle to engineering problems, and full details of the practical computation.

I am, Gentlemen,
Yours faithfully,
G. TEMPLE.

King's College, London.
November 21st, 1932.

VIII. *On the Equilibrium between Radiation and Matter in the Universe.* *By* A. GANGULI *.

Section 1.

IN a previous paper [1] a statistical equilibrium between the number of photons in the free (gaseous) state and that bound or absorbed by matter, for black-body radiation, was considered, and Planck's distribution law in its original and modified form was deduced. During recent years an entirely different kind of equilibrium between radiation and matter has been studied by several authors [2]. This deals with a kind of reaction, in which matter is annihilated and converted into radiation, and reminds one of the more familiar photochemical reactions. The recent discovery of cosmic rays, having energy corresponding to that of hydrogen and helium atoms, lends a strong support to the annihilation theory. The problem is of immense interest, and in fact as early as 1904, Jeans [3] suggested the annihilation of matter as the source of stellar energy. It has now been pretty nearly established that the dwarf stars are derived from stars of large masses. It may be pointed out, however, that Millikan [4] postulates that cosmic rays are not due to annihilation of protons, but the combination of four hydrogen atoms to form helium within the stars, a process accompanied by loss of mass, which corresponds to the

* Communicated by Dr. K. C. Kar.

energy of the most abundant cosmic rays ($\lambda = \cdot 00041$ A.). It is, however, out of place here to enter into the discussion of various theories of the evolution of the universe.

According to the original formula of Stern, derived from thermodynamical principles, the number of molecules of matter (hydrogen atoms) in equilibrium with radiation

$$n = \frac{(2\pi mk\mathrm{T})^{3/2}}{h^3} e^{-\frac{mc^2}{k\mathrm{T}}}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

m being the mass of the hydrogen atom and π, k, T, h, and c having their usual significance. It follows from equation (1) that unannihilated molecules are so few that practically all the matter is converted into radiation. Thus there should be some process of conversion of radiation into matter, in order to account for the sufficiently large amount of matter in the universe. Tolman [5] tries to overcome this difficulty by suggesting a general formula

$$n = b\mathrm{T}^{3/2} e^{-\frac{mc^2}{k\mathrm{T}}} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

on the basis of the first two laws of thermodynamics. The constant b can be evaluated by the Sackur-Tetrode formula for absolute entropy and then (2) becomes identical with (1). Tolman, however, questions the validity of the third law in this particular case and proposes a much larger value of b. But this sems to be rather arbitrary.

A mechanism of conversion of radiation into matter may be conceived of as follows:—The energy of radiation obtained from hydrogen atom

$$h\nu = mc^2,$$

or $$\nu = 2{\cdot}2 \times 10^{23} \quad \text{or} \quad \lambda = {\cdot}0000121\,\text{Å}.$$

The corresponding temperature will be 10^{12}. So Donnan (*l. c.*) proposes that annihilation can take place only at this temperature. At lower temperature radiation is converted into matter, and it is quite probable that ordinary cosmic rays ($\lambda = \cdot 00041$ Å.), which are of stellar origin, are converted into matter, giving nebulæ and subsequently the stellar universe. Thus the small value of n calculated from Stern's equation (1) should offer no difficulty. The stars are converted into radiation, part of these radiations travel to the outer atmosphere, and, due to Compton scattering, the frequency of radiation may be diminished, giving cosmic rays which have less energy, and hence are converted back into matter.

Another controversial point is whether neutral matter or the protons and electrons from matter are converted into

radiation. Equation (1) of Stern deals with the annihilation of neutral hydrogen atom. J. J. Thomson [6], Donnan (*l. c.*), Kassel (*l. c.*), and others, however, believe that the protons and electrons are neutralized, and thus give radiation according to the scheme

$$\mathrm{H} \rightleftharpoons \mathrm{E} + \mathrm{P} \rightleftharpoons \text{radiation.}$$

Kassel treats the problem according to Dirac's theory of protons, and obtains the Stern equation in the following modified form

$$n = 2\frac{(2\pi(m\mathrm{M})^{1/2}k\mathrm{T})^{3/2}}{h^3} e^{-\frac{(\mathrm{M}+m)c^2}{k\mathrm{T}}} \quad . \quad . \quad . \quad . \quad (3)$$

where M and m are the masses of protons and electrons respectively. The above equation can, however, be obtained by the following simple procedure. We take the free energy of a proton as equal in magnitude, but opposite in sign, to that of an electron [7]. It thus follows for the non-degenerate case (owing to the high temperature of the stars), from the generalized Gibbs's Statistics [8], considering the total energy of proton as $\mathrm{E}_1 + \mathrm{M}c^2$ and that of electron as $\mathrm{E}_2 + mc^2$ and $\Phi = \mathrm{N}h^3$, where N is the total number, the number of electrons

$$\mathrm{N}_1 = \frac{\mathrm{N}}{\Phi} \mathrm{V} 2\pi(2m)^{3/2} \int_0^\infty \frac{\mathrm{E}_1^{\frac{1}{2}} d\mathrm{E}}{e^{-\frac{\psi + \mathrm{E}_1 + mc^2}{k\mathrm{T}}} + 1}$$

or

$$\frac{\mathrm{N}_1}{\mathrm{V}} = n_1 = \frac{(2\pi mk\mathrm{T})^{3/2}}{h^3} e^{-\frac{mc^2 - \psi}{k\mathrm{T}}}, \quad . \quad . \quad . \quad . \quad (4)$$

and similarly the number of protons

$$n_2 = \frac{(2\pi \mathrm{M}k\mathrm{T})^{3/2}}{h^3} e^{-\frac{\mathrm{M}c^2 + \psi}{k\mathrm{T}}} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Now in order to maintain electrical neutrality we must have $n_1 = n_2$. Hence from equations (4) and (5) we have

$$e^{\frac{\psi}{k\mathrm{T}}} = \left(\frac{\mathrm{M}}{m}\right)^{3/4} e^{-\frac{(\mathrm{M}-m)}{2k\mathrm{T}} \cdot c^2} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Substituting the value of $e^{\frac{\psi}{k\mathrm{T}}}$ in equation (4) or (5) we have

$$n = n_1 = n_2 = \frac{(2\pi(m\mathrm{M})^{\frac{1}{2}}k\mathrm{T})^{3/2}}{h^3} e^{-\frac{(m+\mathrm{M})}{2k\mathrm{T}} c^2}, \quad . \quad (7)$$

which is the formula of Kassel without the factor 2.

Section 2.

In the previous section we have considered the annihilation of electrons and protons separately; but Jauncy and Hughes (*l. c.*) argue that an electron and a proton present separately could not be converted into radiation, since for this case the following conditions must be fulfilled :—

(*a*) Conservation of energy.

(*b*) Conservation of momentum.

(*c*) Conservation of charge.

(*d*) Reversibility of the process.

(*e*) Velocity never to exceed that of light.

On examining these it is evident from the above that there is no difficulty as regards (*a*), (*c*), (*d*), and (*e*), since conservation of energy and charge has been maintained, and reversibility of the process has been suggested, and nowhere has it been assumed that the velocity would exceed that of light. But difficulties arise is connexion with condition (*b*). Let us therefore consider now the possibility of conversion of neutral atom into radiation.

We may consider the problem from two aspects. Firstly, following a method of a previous paper [9], corresponding to thermal ionization, we consider an equilibrium between free matter and bound matter (which is converted into radiation), and thus we have the number of free atoms (gas)

$$N_1 = \frac{NV}{\Phi} \frac{(2\pi mkT)^{3/2}}{h^3} e^{\frac{\psi}{kT}} \quad . \quad . \quad . \quad . \quad (8)$$

and the number of bound atoms

$$N_2 = \frac{N}{\Phi} B h^3 e^{-\frac{mc^2+\psi}{kT}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where mc^2 is the potential corresponding to the ionization potential, *i. e.*, it is the energy lost by matter in going to the bound state (in the process of conversion into radiation). Since $N_1 = N_2$ we have the concentration of matter in equilibrium with radiation,

$$n = \frac{(2\pi mkT)^{3/2}}{h^3} e^{-\frac{mc^2}{kT}}. \quad . \quad . \quad . \quad . \quad (10)$$

Section 3.

In this section we shall consider the problem afresh from the point of relativity. A simple procedure will be to find

the number of atoms present by the direct method. Since matter is in equilibrium with radiation, the total number of hydrogen atoms is not constant, hence the free energy of matter may be taken to be zero[10]. Again, in using the generalized Gibbs's Statistics, we shall incorporate the relativistic expression for mass and momentum. Thus we have the number of atoms in equilibrium per unit volume

$$n = \frac{N}{\Phi}\int \frac{dp_x\,dp_y\,dp_z}{e^{\frac{mc^2}{kT}\sqrt{1+p^2/m^2c^2}}+1}, \quad \ldots \quad (11)$$

where $mc^2\sqrt{1+p^2/m^2c^2}$ is the energy.

Now since

$$p_x^2+p_y^2+p_z^2=p^2 \quad \text{and} \quad \Phi=Nh^3,$$

we have

$$n = \frac{4\pi}{h^3}\int \frac{p^2dp}{e^{\frac{mc^2}{kT}\sqrt{1+p^2/m^2c^2}}+1}. \quad \ldots \quad (12)$$

Now for $e^{\frac{mc^2}{kT}} >> 1$ (non-relativistic case)

$$\frac{p^2}{m^2c^2} = \frac{m_0^2c^2\beta^2}{(1-\beta^2)m_0^2c^2} = \frac{\beta^2}{1-\beta^2} << 1, \qquad \left(\beta=\frac{v}{c}\right).$$

Hence

$$\sqrt{1+p^2/m^2c^2} = 1+\tfrac{1}{2}p^2/m^2c^2$$

and

$$mc^2\sqrt{1+p^2/m^2c^2} = mc^2+p^2/2m.$$

Therefore, from equation (12),

$$n = \frac{4\pi}{h^3}\int \frac{p^2dp}{e^{\frac{mc^2+p^2/2m}{kT}}+1}. \quad \ldots \quad (13)$$

For non-degenerate case

$$n = \frac{(2\pi mkT)^{3/2}}{h^3}\, e^{-\frac{mc^2}{kT}}, \quad \ldots \quad (14)$$

which is the Stern equation (1).

For $e^{\frac{mc^2}{kT}} << 1$ (relativistic case) $p^2/m^2c^2 >> 1$, and hence

$$mc^2\sqrt{1+p^2/m^2c^2} = \frac{mc^2p}{mc} = pc.$$

Hence, from the equation (12),

$$n = \frac{4\pi}{h^3}\int_0^\infty \frac{p^2 dp}{e^{pc/kT}+1}$$

$$= \frac{4\pi(kT)^3}{c^3h^3}\cdot\int_0^\infty \frac{x^2dx}{e^x+1}, \qquad \text{where } x = pc/kT,$$

$$= \frac{8\pi k^3T^3}{h^3c^3} \qquad (e^x >> 1). \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

It is interesting to note that for the relativistic case the number of atoms in equilibrium is independent of the mass. In fact this is equal to the number of quanta (assuming this to be isotropic), for it follows from the previous paper (Ganguli, *l. c.*) that the number of quanta per unit volume in any direction

$$n_1 = \frac{4\pi}{c^3}\int \frac{\nu^2}{e^{\frac{h\nu}{kT}}-1}\, e^{-\frac{h\nu}{kT}}d\nu$$

$$= \frac{8\pi k^3T^3}{h^3c^3} \quad \text{for} \quad e^{\frac{h\nu}{kT}} >> 1.$$

It thus follows that when matter attains the velocity of light it is indistinguishable from radiation, and then the laws of black-body radiation holds good. In fact we get the Stefan–Boltzmann law by multiplying the number of atoms given by equation (15) with the energy kT of a single atom.

Section 4.

By a reverse process the Stern formula can be obtained from the radiation law. We have, as before, the number of quanta having frequency between ν and $\nu+d\nu$ (considering only one kind of polarization),

$$dn = \frac{4\pi\nu^2}{c^3}\, e^{-\frac{h\nu}{kT}}d\nu \qquad \left(e^{\frac{h\nu}{kT}} >> 1\right). \quad . \quad . \quad . \quad (16)$$

If we substitute mc^2 for $h\nu$ and also $E = h\nu$, we have

$$dn = \frac{4\pi m^{3/2}}{h^3}\, E^{\frac{1}{2}}\, e^{-\frac{E}{kT}}dE. \quad . \quad . \quad . \quad . \quad (17)$$

Now in the case when matter has the velocity of light it is entirely converted into radiation and its rest energy $E_0 = h\nu$. For ordinary matter whose velocity is smaller than that of light, however, the energy $E = E_0 + E'$, where E' is the kinetic energy, and substituting this new value of E in equation (17), and integrating, we have again

$$n = \frac{(2\pi mkT)^{3/2}}{h^3}\, e^{-\frac{mc^2}{kT}}. \quad . \quad . \quad . \quad . \quad (18)$$

We thus have four different cases:—(1) In ordinary chemical equilibrium the rest energy of the atoms and molecules remain unaffected, and the mass is unchanged. (2) In the second case of equilibrium between matter and radiation, when the rest energy of the matter is unchanged, we have simply the laws of black-body radiation. (3) At high temperature ($T = 10^{12}$) the matter is mostly converted into radiation, and when it attains the velocity of light it is converted entirely into radiation, and then the total energy can be expressed by the Stefan–Boltzmann law ($h\nu = kT = mc^2$). (4) In the outer atmosphere of the stellar system the velocity of radiation becomes diminished, *i. e.*, radiation is converted into matter.

Conclusion.

In conclusion we may note that some authors[11] have very recently proposed the existence of neutrons, which have mass of the hydrogen atom, the valency electron of the latter being enclosed into the nucleus. These neutrons have very high penetrating power and behave like cosmic rays of wave-length given by the relation $\left(\lambda = \frac{h}{mv}\right)$. According to L. de Broglie's theory this corresponds to the wave-length of hydrogen atom moving with the velocity comparable to that of light. If we follow the procedure of Section 3 it is immaterial whether matter is annihilated and converted into radiation or into neutrons; we will have the same value of n. We are at present not in a position to choose between these two theories. The latter hypothesis may be fruitful in the conversion of neutron into ordinary hydrogen, and this may not be so startling as the conversion of radiation into matter. It is, however, difficult to conceive of a hydrogen-atom wave of velocity of light existing as matter. We get, under these circumstances, the number of atoms in equilibrium to be the same as the number of quanta obtained from Planck's law.

Summary.

Annhilation of matter and its conversion into radiation has been studied from two different points of view. The neutralization of proton and electrons with the emission of radiation gives a formula similar to that of Kassel. The equilibrium of neutral matter and radiation gives for the non-relativistic case the formula of Stern, while for the relativistic case the number of material atoms in equilibrium becomes independent of mass, and is identical with the number of quanta.

Thus, when the matter moves with the velocity of light it becomes identified with radiation. Similarly the reverse process of conversion of radiation into matter is suggested, and starting from Planck's law the Stern formula is obtained It is suggested that at temperatures of the order 10^{12} within the star most of the material atoms are converted into radiation. On the other hand, the cosmic rays outside the stellar atmosphere, where the temperature is low, is partly converted into matter. The possibility of conversion of hydrogen atom into neutron is briefly discussed.

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(5) Tolman, *loc. cit.*
(6) Thomson, Phil. Mag. xliii. p. 737 (1924).
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(8) Kar and Mazumdar, *Z. f. Phys.* lv. p. 546 (1929).
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May 1932.

IX. *A Direct Current Amplifier.* By P. A. Macdonald, *Ph.D., Assistant Professor of Physics, and* Jean T. Macpherson, *University of Manitoba* *.

IMPRESSING a potential difference between the control grid and filament of a thermionic tube causes a change in the plate current of the tube. The algebraic expression for this sensitivity to voltage is

$$S_v = G_m S_g, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

* Communicated by the Authors.

where S_v is the voltage sensitivity, S_g the sensitivity of the meter in the plate circuit, and G_m the mutual conductance of the tube, that is the slope of the curve relating the grid potential E_g to the plate current I_p. In using the thermionic tube to amplify direct currents it is customary to force the input current through a high resistance shunted between the control grid and filament of the tube so that the resulting drop in potential raises the potential of the grid relative to the filament, the change in plate current being then observed, and used as a measure of this potential. The sensitivity of such a system to current will be

$$S_c = G_m S_g R, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

S_c being the current sensitivity and R the value of the resistance employed, which, of course, must be small relative to the natural resistance existing between the filament and the grid. The magnitude of the plate current places a lower limit upon the magnitude of the input current which can be detected, since the amplified current must be sufficiently large to record on a meter not too delicate to register the plate current.

Considerable increase in sensitivity may be obtained by introducing into the simple circuit an auxiliary battery * in such a manner that it forces a current through the plate current meter equal to the plate current, but in the opposite direction. S_g may then be increased until irregularities in the plate current render the zero point unsteady. If the plate current from a second vacuum tube be substituted for the current due to the auxiliary battery, the fluctuations occurring in the two tubes may be made to offset each other to a considerable extent, allowing further increase in S_g to be made. Using commercial thermionic tubes designed for the reception of radio broadcasting a voltage sensitivity of 10^{-5} volt/mm. has been reported for a two-tube balanced circuit with a current sensitivity somewhat greater than 10^{-14} amp./mm. †. Metcalf and Thomson ‡ have designed a special tube for direct current amplification, known as the General Electric FP 54, two of which have been used by Du Bridge § in the balanced circuit to give a voltage sensitivity of 4×10^{-6} volt./mm.

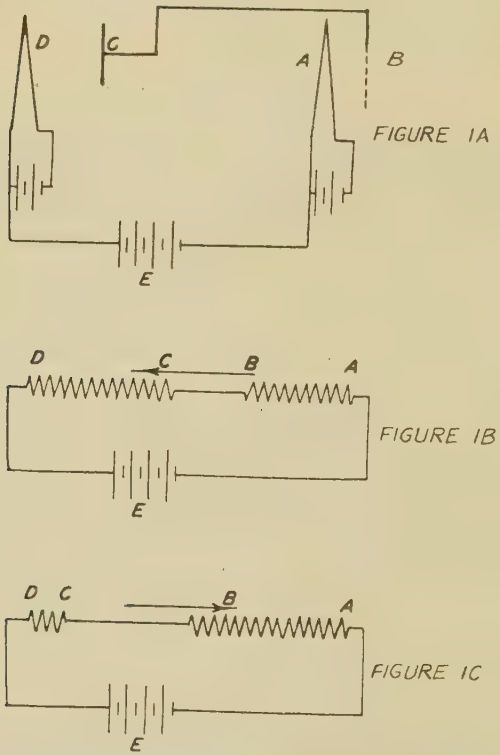
The above two methods of balancing out the plate current enable S_g in equation (1) to be increased, the quantity G_m,

* Razek and Mulder, J. O. S. A. & R. S. I. vol. i. p. 461 (June 1929).
† Razek and Mulder, J. O. S. A. & R. S. I. vol. i. p. 402 (Dec. 1929).
‡ 'Physical Review,' Nov. 1, p. 1489 (1930).
§ L. A. Du Bridge, Phys. Review, Feb. 15, p. 393 (1931).

however, remaining constant. It is the purpose of this communication to describe a circuit in which G_m has been increased and S_g kept constant.

The phenomenon upon which the authors have based what they believe to be a new circuit is that the direction of flow of the grid current alters at a definite value of the grid potential. The grid current of a UX 112 A General Electric

Figs. 1 A–1 C.



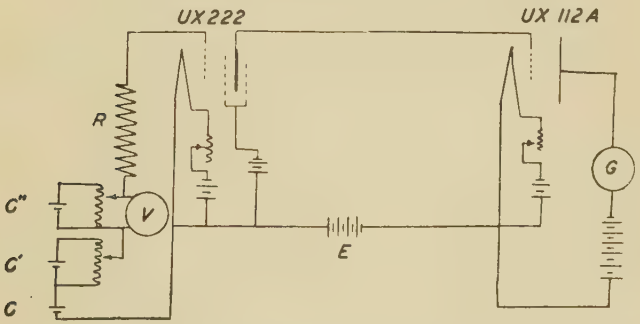
Showing the manner by which the unidirectional conductivity of an auxiliary vacuum tube may be made to alter the potential of the grid of a triode when its grid current changes direction.

tube is shown graphically in fig. 4 as a function of the grid potential. It will be seen that at a potential of the grid of −0·33 volts, relative to the negative side of the filament, the grid current is zero. With more positive values, the electron flow is from the filament to the grid, while with greater negative potentials the direction of flow is reversed. This

phenomenon is due to a flow of positive ions to the grid and the repulsion by it of the filament electrons.

Suppose, now, that a circuit be set up as in fig. 1 A, where AB represents the filament and grid of the above tube, and CD the plate and filament of a second tube which will allow electrons to flow from D to C, but not in the reverse direction. If the potential of B is greater than $-0{\cdot}33$ volts the direction of current flow will be that of fig. 1 B, since the electrons flow from the filament A to the grid B and encounter the maximum resistance between the plate C and filament D. However, if B is given a potential less than $-0{\cdot}33$ volt, the current is reversed in direction, the positive ions flowing to the grid being equivalent to a flow of electrons from the grid B to the filament A. The resistance of DC to electrons moving in this direction is relatively low, while that of BA

Fig. 2.



Wiring diagram of complete amplifier.

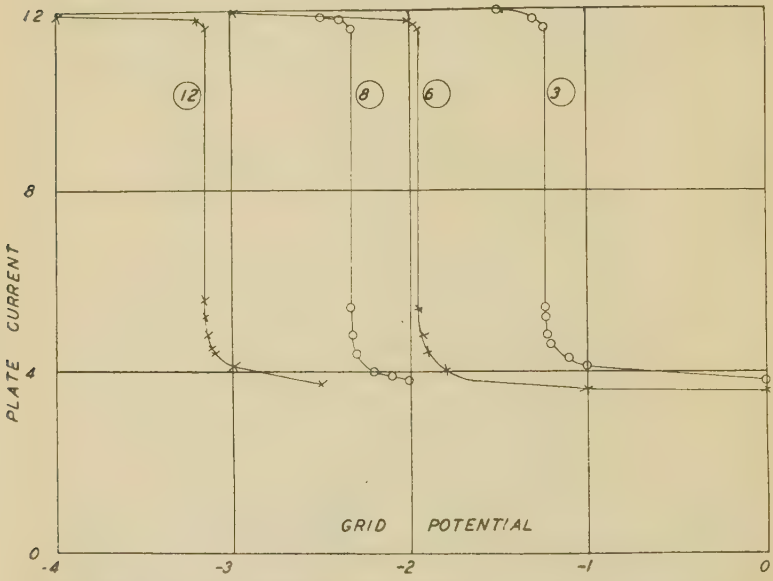
is increased. Thus in fig. 1 B the major drop in potential of the battery E is across DC, while in fig. 1 C it is practically all impressed between the grid and filament of the first tube. The manner in which a small potential change at B may control the location of the potential drop due to E in such a circuit has been investigated by the authors, with the result that a stable amplifier of high voltage sensitivity has been obtained.

The first circuit examined contained a UX 112 A three-element tube with the grid connected through a UX 222 four-element screen-grid tube in the manner of fig. 2. The 112 A tube corresponded to the tube AB of fig. 1 A and will be referred to hereinafter as the "plate tube," the 222, corresponding to CD, being called the "grid tube." The following properties of this circuit were determined empirically.

(1) *The negative potential of the control grid of the plate tube is directly proportional to the potential applied at* E.

A variable source of potential and a voltmeter were substituted for the steady E battery and the plate current of the plate tube determined for various potentials, these readings being reduced, in turn, to grid potentials from the grid potential *vs.* plate current characteristic of the tube. The resulting data when plotted demonstrated the expected linear relation.

Fig. 3.



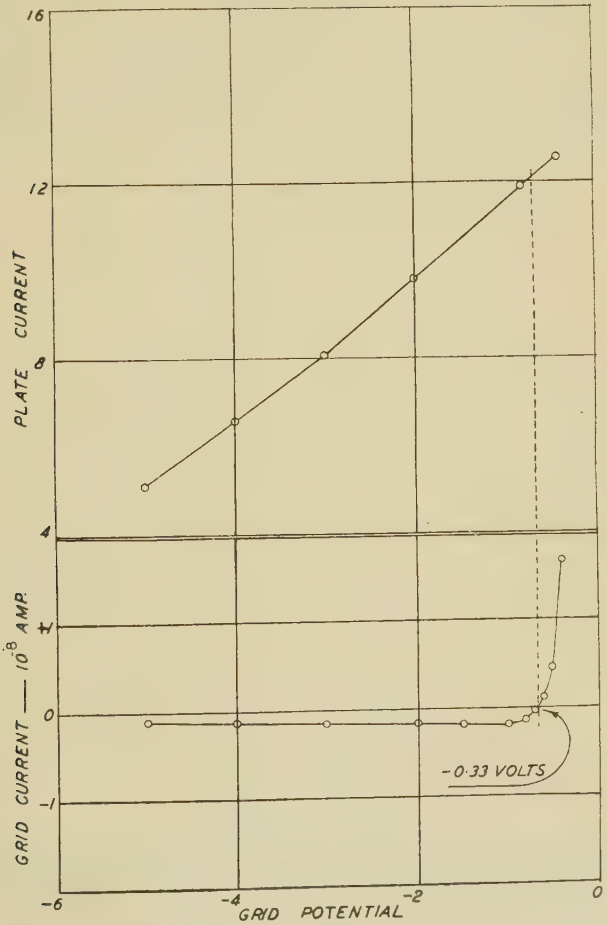
Curves showing the relation existing between the grid potential of the input tube and the plate current of the output tube. The encircled numbers give the values of the screen-grid potentials at which the curves were run.

(2) *The plate current may be controlled by the potential of the control grid of the grid tube.*

The data relating the grid potential of the grid tube to the plate current of the plate tube are plotted in fig. 3. The family of curves given are taken for various values of the screen-grid potential. These curves, when examined in conjuction with those of fig. 4 giving the standard characteristics of the plate tube, demonstrate clearly the switching of

the drop in the E battery potential from the grid tube to the plate tube as the positive ion current replaces the electron grid current.

Fig. 4.



The operating characteristics of a 112 A triode. The plate currrent is measured in milliamps. It will be seen that at a current slightly in excess of 12 milliamps the grid current changes its direction of flow.

(3) *The negative bias of the control grid of the grid tube, at which the mutual conductance of the unit is a maximum, is directly proportional to the screen-grid potential.*

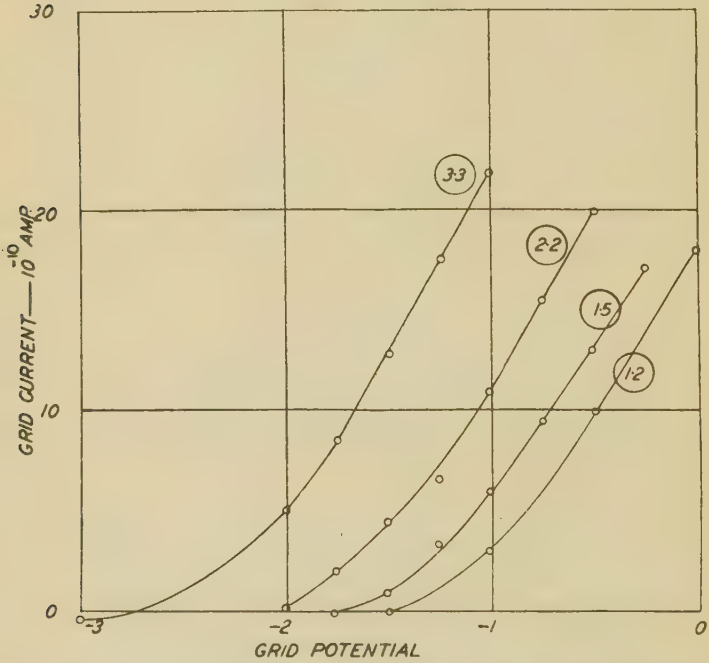
The data relating the position of maximum mutual conductance to the negative bias of the control grid were obtained

from fig. 3, and when plotted against the corresponding screen-grid potentials showed a linear relation.

(4) *The grid conductance of the grid tube is for practical purposes independent of the screen-grid potential.*

The grid conductance or slope of the curve relating the grid potential to the grid current of the grid tube was examined for various control grid potentials using a sensitive

Fig. 5.



Curves showing the effect on the grid current of decreasing the filament current of a UX 222 four-element tube. The encircled numbers indicate the filament voltages.

galvanometer in the control grid circuit. The results showed that the screen-grid potential could be varied over a wide range without appreciably altering the point of inflexion of the curve.

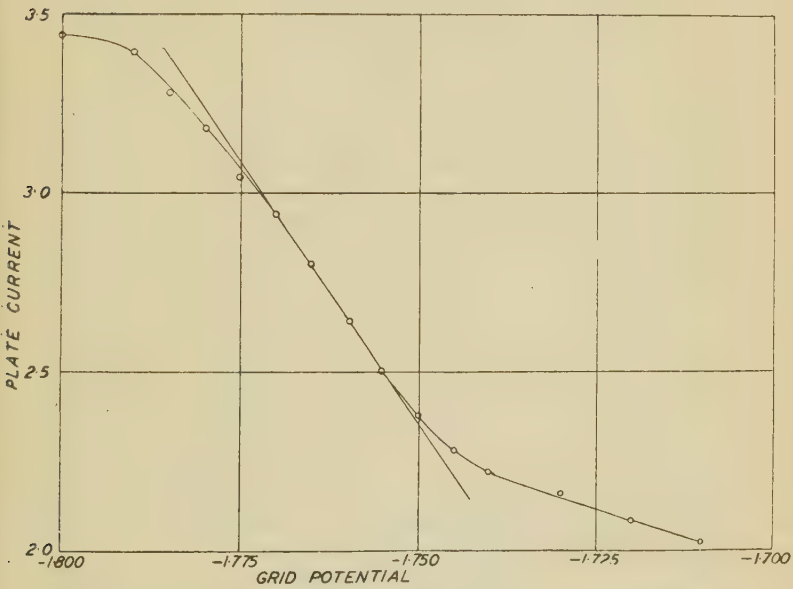
The Unit as a Current Amplifier.

The foregoing data are sufficient to allow the properties of the unit as a direct current amplifier to be determined.

In order that a high sensitivity to current be obtained the grid conductance must be a minimum and the mutual conductance a maximum ; that is, the input current must raise the potential of the grid as much as possible, and this in turn must alter the plate current to the maximum extent.

The grid conductance curve of the amplifying unit will be the grid conductance of the grid tube which is reproduced for different filament voltages in fig. 5. The filament voltage employed in securing the above data was 1·2 volts, so that the grid conductance is a minimum with a bias more negative

Fig. 6.



The plate current characteristic of the final amplifier. The linear region may be increased by increasing the E battery potential.

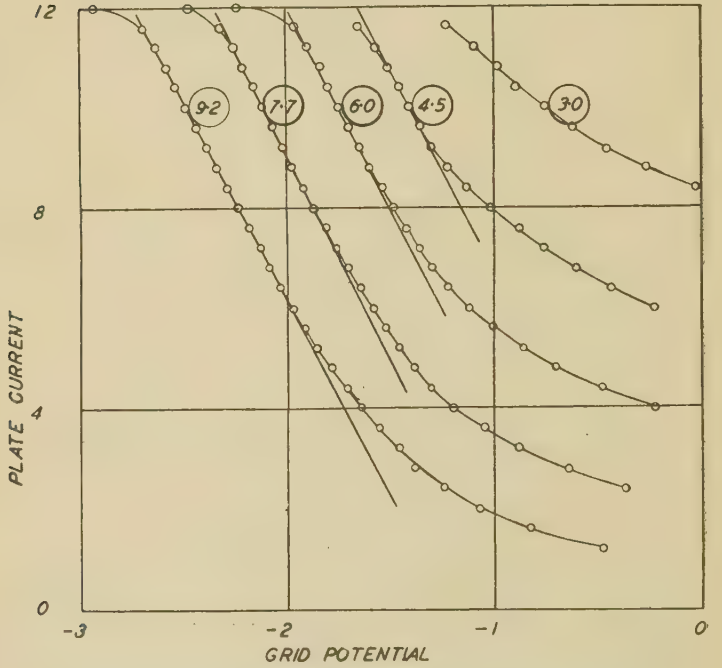
than −1·5 volts. The bias at which the mutual conductance of the unit is a maximum is given the same value by adjusting the screen-grid potential. In practice the easiest method of adjustment is to use a constant battery C (fig. 2) for the grid bias, adjust the screen grid to approximately the correct value, and then use a potentiometer C′ to bring grid potential to the correct working point.

The curves of fig. 3 show a mutual conductance too great to enable stability to be obtained, but the slope may be

controlled by either the plate or filament potentials of the plate tube. In fig. 6 a curve is reproduced which was obtained with 90 volts on the plate and a 3·5 volt drop in potential across the filament of the 112 A tube.

The measured slope of this graph shows a voltage sensitivity of 3×10^{-4} volt./mm. which, with the input resistance of 2×10^{8} ohms, gives a current sensitivity of $1{\cdot}5 \times 10^{-13}$ amp./mm.

Fig. 7.



The plate current characteristic of a direct current amplifier. The encircled values are those of the E battery potentials.

for the system. The instrument is extremely stable at this sensitivity having a drift of only 34 mm. in five hours, after equilibrium has first been established. The overall amplification is with this set-up 10^{8}, and an ordinary voltmeter may be used as the plate current meter, thus giving a rugged instrument that may be readily transported. No particular shielding is necessary, except, of course, with the grid system,

which is readily obtained by placing the two tubes in a grounded metal box. The instrument is sensitive to sunlight, probably due to the liberation of photoelectrons from the grid system, and care must be taken to see that no light falls on the tubes.

In addition to the above unit other types of tubes have been examined and a satisfactory amplifier of less sensitivity obtained using a UX 222 as a triode by connecting the screen grid to the plate and using a 201 A or 112 A as the plate tube. A family of grid potential *vs.* plate current curves for this system at different E battery potentials is given in fig. 7. These curves show a section with a true linear relation the extent of which is a function of the E battery potential. The shift of the curves to regions of greater negative bias of the grid tube with increase in the potential at E is of practical importance allowing the region of linear mutual conductance to be brought into coincidence with the minimum grid conductance. The filament potential of the grid tube allows a certain control of the grid current of this tube to be obtained, as will be seen from fig. 5. From these curves one concludes it to be desirable to operate the filament at a minimum voltage, both to decrease the necessary negative bias, and lessen the drain on the filament battery. This filament voltage has been found to make no difference to the mutual conductance of the unit.

The high degree of stability shown by this type of amplifier would allow greater sensitivity to be obtained using the method of increasing S_g described at the beginning of this communication. Further work is now being undertaken to see just how far the sensitivity can be increased, but the material presented in this paper indicates a method of constructing direct current amplifiers, which will be mechanically rugged and have a sensitivity in the neighbourhood of 10^{-13} amp./mm.

This work has been carried out in the Radium Laboratory of the Manitoba Cancer Relief and Research Institute, established in the Department of Physics, University of Manitoba, and the authors would like to express their thanks for the courtesies of these institutions.

The Department of Physics,
University of Manitoba.

X. *The Maximum Rate of Evaporation of Water.* *By* T. Alty, *D.Sc., Ph.D., Research Professor of Physics, University of Saskatchewan*.*

Introduction.

THE mass (m grams.) of gas striking unit area of a surface per second may be calculated with the aid of Knudsen's formula [1]

$$m = 43{\cdot}75 \times 10^{-6}\, P\sqrt{\frac{M}{T}} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In this formula P is the pressure of the gas in dynes per square centimetre, M the molecular weight of the gas, and T its absolute temperature.

The maximum rate of evaporation of a solid or liquid, *i. e.*, the rate of evaporation into a complete vacuum, may be calculated from equation (1), since in the case of a substance in a state of equilibrium with its saturated vapour, the mass leaving the substance per second and entering the vapour must be exactly balanced by the mass striking the substance from the vapour and leaving the vapour phase. Now, if the vapour-pressure at the temperature of the experiment is sufficiently small, the mass leaving unit area per second will be affected only very slightly by the presence of the vapour in the surrounding space, so that under these conditions we may say:

Maximum rate of evaporation of any substance,

= mass evaporating into a perfect vacuum per second,

= mass leaving the substance and entering its saturated vapour per second,

= mass returning to the substance from the saturated vapour per second,

= mass of saturated vapour striking unit area of the surface per second × fraction (f) of incident molecules which are able to remain on the surface

$$= 43{\cdot}75 \times 10^{-6}\, P\sqrt{\frac{M}{T}} \cdot f \text{ gram/sq.cm./sec.} \quad . \quad (2)$$

It is, therefore, possible by comparing the rate of evaporation deduced from (2) with that measured experimentally to determine the value of the evaporation coefficient f. Such comparisons have already been made in a number of cases.

* Communicated by the Author.

Langmuir [2] has shown that in the case of the evaporation of tungsten from a tungsten wire, the value of f is very close to unity, so that in this case there is practically no reflexion of the vapour-molecules incident on the surface.

Knudsen [1] has examined the rate of evaporation of liquid mercury and has observed that the value of f is very sensitive to the presence of small traces of impurity in the evaporating surface. For a newly-formed clean mercury surface he concluded that in this case also the value of f was very close to unity.

Apart from Knudsen's experiments, little work has been carried out on the measurement of f for liquids. For most liquids the vapour-pressure is much greater than that of mercury at the temperature of experiment, and it is difficult to reduce the pressure sufficiently to obtain the conditions for evaporation into a vacuum. For this reason formula (2) must be slightly modified when considering the evaporation of a liquid into a space in which the vapour-pressure (p) is less than the saturated vapour-pressure, but is not zero. In this case it appears that the net mass evaporated is equal to the mass leaving the liquid reduced by the mass returning to it from the vapour

$$=43{\cdot}75\times10^{-6}(\mathrm{P}-p)f\sqrt{\frac{\overline{\mathrm{M}}}{\mathrm{T}}}\ \text{gram/sq. cm./sec.} \quad . \quad (3)$$

The value of f can then be deduced as before by comparison of (3) with the experimentally measured rate of evaporation. In order to obtain results of value, p must be small, so that the amount of vapour present above the liquid is not sufficient to influence appreciably the rate at which molecules leave the liquid.

Work of this nature has been performed on carbon tetrachloride and water by Alty [3] and Alty and Nicoll [4]. The low heat conductivity of these liquids increases in one respect the difficulty of measuring the true value of f. In the case of the metallic elements the rates of evaporation examined are so low and the heat conductivity so high that the evaporation produces no important temperature differences in the mass of the material. In the case of water, however, the very rapid evaporation produces intense local cooling in the surface, so that for water at 25° C. the temperature of the surface may be 20° C. to 30° C. below that of the liquid as a whole. This temperature difference is of great importance in the calculation of f, since the pressure P entering into equation (3) is the saturated vapour-pressure at the *temperature of the surface*. An error in the measure-

ment of the surface temperature will thus lead to a considerable error in the value of P, the saturated vapour-pressure, and so also in the value of f.

In the earlier experiments on carbon tetrachloride and water, the surface temperature of the evaporating liquid was measured by means of a thermocouple immersed in the liquid. As the latter evaporated, the thermocouple passed through the surface, and so made possible an estimate of the surface temperature. This surface temperature is clearly a function of the vapour-pressure p above the liquid surface, being lower the smaller the pressure of the vapour. The temperature difference between the surface and a thermostat was therefore measured as a function of the pressure p, and the resulting graph was extrapolated to $p=0$, to give the surface temperature corresponding to evaporation into a vacuum. In the same manner, the rate of evaporation was measured as a function of p, and the corresponding graph gave the rate of evaporation into a vapour-free space. From these results the rates of evaporation of carbon tetrachloride and water were calculated by equation (2), and the results for carbon tetrachloride indicated a value of f near to unity.

However, in the case of water this was not so, the values of f ranging from $f=0{\cdot}01$ to $f=0{\cdot}02$. Unless these values are very considerably in error, it appears that not all the incident water vapour molecules striking the liquid surface are able to enter.

In view of the unexpected nature of this result the problem has now been investigated by a different method, and the present paper deals with the results so obtained. It may here be stated that these new results still indicate a considerable discrepancy between the experimental and theoretical rates of evaporation of water and give values of f ranging between 0·035 and 0·045.

From the above discussion it appears that the two quantities involved in the determination of f, which must be measured with as much accuracy as possible, are :

(1) the mass evaporating per second ;
(2) the temperature of the actual surface.

As regards the mass measurement, the earlier experiments were quite accurate, the mass evaporating being measured directly by the loss in weight of the small containing vessel. The method of measuring the surface temperature was not so accurate. Any instrument introduced into the surface cannot do more than measure the *average* temperature of a thin layer near the surface, and this average temperature must be, of necessity, higher than the temperature of the

actual evaporating surface layer. It therefore appears that the surface temperatures obtained by means of the thermocouple were too high. Consequently the values of P and T used in the earlier experiments were too great and the values of f derived therefrom were too small. Thus a more accurate estimate of the surface temperature would result in smaller values for P and T, and consequently a larger value for f, and might bring the results for water into better agreement with those for other substances. It will be seen from equation (3) that the derived value of f increases rapidly with decrease of surface temperature. The accurate determination of this temperature is thus essential.

In the present work the surface temperature has been obtained from direct measurement of the surface tension of the evaporating surface. As the surface tension must be controlled by the temperature of the outermost layers of liquid molecules, the temperature thus derived should be a very close approximation to the actual quantity required in the work. The measurement of the temperature by this means has the additional advantage that it eliminates the necessity of introducing into the surface any foreign body which could by its presence alter the temperature distribution there. The temperature was deduced from the surface tension by means of the data collected by Young and Harkins [5].

The surface tension was measured by the drop-weight method of Harkins and Brown [6]. Drops of air-free distilled water were allowed to form slowly on a specially prepared tip in an evacuated space. Evaporation thus progressed steadily at the surface of the growing drop, whose surface temperature was thereby considerably reduced. The surface tension (γ) was derived from the drop weight (m grams) in the usual manner by the formula of Harkins and Brown (*loc. cit.*).

$$\gamma = \frac{mg}{2\pi r f(r/V^{1/3})} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Here V is the drop volume and r is the radius of the dropping tip. $f(r/V^{1/3})$ is a correction term whose values are tabulated by Harkins and Brown.

On substituting in (4) the radius of the actual glass tip used, it was found that over the range required the relation between the surface tension and the drop-weight could be represented by the more convenient approximate formula

$$\gamma = -2{\cdot}217 + 1{\cdot}3480m - 3{\cdot}7283 \times 10^{-3}m^2 + 1{\cdot}3719 \times 10^{-5}m^3. \quad . \quad . \quad . \quad (5)$$

The surface temperatures measured from the surface tension in this manner were consistently lower than those measured by the thermocouple in the earlier work. The difference, however, was not so great as might have been expected and, as was indicated in a recent note [7], increased the value of f for water only from 0·01–0·02 to 0·035 – 0·045, values which are still very far from unity.

Experimental.

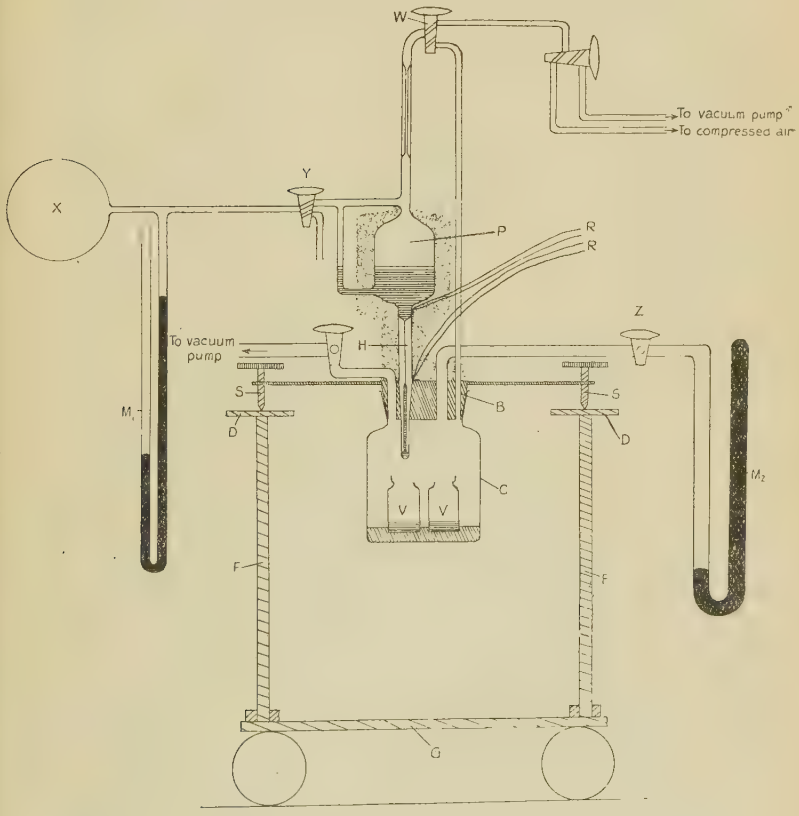
The glass tip on which the drops were formed was constructed in the manner described by Harkins and Brown. A piece of glass capillary tubing was inserted in a lathe and ground on a carborundum plate until its cross-section was accurately circular. The ground surface was then carefully repolished after the end of the capillary had been ground flat and perpendicular to the length of the circular tube. The polishing was continued until the circular end of the glass tube was free from flaws when examined under a low-power microscope. The end was left slightly rough to ensure that the water would wet it and flow over the whole end of the tube.

This tip was sealed to the lower end of a piece of fine thermometer tubing H (fig. 1) which formed the lower outlet of a glass pipette P which contained the water. The thermometer tubing offered such resistance to the flow of water from the pipette that one drop was formed in about eight minutes when the pipette was open to the atmosphere.

The pipette was ground into a massive block (B) of brass which served to control the temperature of the water flowing from the pipette, and also acted as a ground stopper for the container C into which the drops fell. This brass block was supported by three levelling screws S which rested on a flat annular stand D. This arrangement, resting on the three rigid bars F, facilitated the levelling of the polished tip, and at the same time gave ample space for the manipulation of the containing vessel C below the tip. The upper end of the pipette was connected to a two-way stopcock W. One of the arms of this cock led back into the container C and the other to a source of compressed air and to a vacuum pump. Thus by manipulating the tap W the pressure above the water in the pipette could be controlled at will and the rate of flow through the thermometer tube made as great as required by increasing the pressure above the water surface. The open manometer M_1, reading up to two atmospheres pressure, gave the pressure above the water surface. In

order to minimise the small change in this driving pressure due to the outflow of water in an experiment, a large volume X was inserted in the system. Two large metal tubes led out through the brass block B, one of them to the manometer M_2 giving the pressure inside the container, and

Fig. 1.



the other to the pumping system by means of which C was evacuated. The pressure in the container C, recorded by M_2 was observed with the aid of a travelling microscope.

In order to maintain the drop-weight apparatus as free from vibration as possible, the stand G was supported on three rubber balls resting on a table whose legs stood on a thick pad of felt. The vibration transmitted from the pumping system was then extremely small.

For the purpose of determining the evaporation coefficient f, it is necessary to measure the temperature of the evaporating surface and also the mass evaporating per second per square centimetre from that surface. This mass was deduced from the rate of flow of water through the thermometer tube H. It is necessary to control the temperature of the tube and also to know this temperature as accurately as possible. For this purpose thermocouples RR were inserted one at each end of the tube H and the whole of the tube and pipette were covered with an insulating layer of asbestos as shown.

The drops themselves were collected for weighing in one of the two small glass vessels VV in the container C. These were fixed in symmetrical positions in C so that either could be brought directly below the dropping tip by rotation of C on its ground stopper. In an experiment, the drops were allowed to fall into one of these vessels until the pressure in C became quite steady with the vacuum pump running. The two small vessels were then interchanged and a counted number of drops allowed to fall into the second one. Their position was then reversed once more, so that any further drops falling while the air was being re-admitted fell into the first vessel. It was necessary to catch *all* the drops in these small vessels in this way in order to prevent water accumulating on the bottom of the container C and then evaporating. Such evaporation from a large area would make it impossible to reduce the pressure (p) in the container C appreciably below the saturated vapour-pressure at the temperature of the evaporating water.

Since the surface tension is to be deduced from the mass of the falling drops it is essential that evaporation from these drops after their fall be prevented. For this purpose the two small collecting vessels VV were partly filled with a light petroleum oil having a very low vapour-pressure. Several oils were tried until one was found which had the necessary small vapour-pressure, and which also allowed the falling drops to sink through it at once, without remaining suspended from the oil surface. The oil used was quite satisfactory and effectively prevented any evaporation from the water below it.

With an arrangement of the type described, it is clear that there need be no evaporation except at the surface of the forming drop itself and that the drop after falling will not be subject to further evaporation As the average drop area was quite small (half-square centimetre approximately) and the capacity of the pump used was large, it was possible to

attain quite small pressures (1·6 mm.) in the system when water at 25° C. was being supplied to the drop. The presence of any water in C naturally increased this minimum pressure considerably.

In order to investigate the variation of the rate of evaporation with the pressure in the container C, the rate of pumping was varied from time to time by inserting tubes of different diameter between the apparatus and the low pressure pump. When working with the pressure in the apparatus considerably below the saturated vapour-pressure at the temperature of the container C (25° C.), the number of drops which could be safely collected in the vessel V was limited by the fact that if too much water collected beneath the oil it began to boil furiously and so sprayed the oil and water mixture over the whole container. In general ten to twelve drops were collected in each experiment at low pressures and the drop weight deduced therefrom. This number could be used without too much time being wasted in recleaning the apparatus.

The water used was redistilled and collected in a pyrex container. It was then thoroughly boiled under reduced pressure and kept sealed from the atmosphere until required. It was also necessary to remove all the air from the oil used in the vessels V which otherwise filled up with large bubbles as soon as the pressure in the apparatus was reduced. The pipette was filled with water by immersing its ground tip in air-free water and connecting its upper end through the tap W with the vacuum pump. It could be rapidly emptied when required by opening W to the atmosphere and evacuating the container C.

Measurement of Tip Radius.

In order to obtain the surface tension of the evaporating surface from the weight of the drops the effective radius of the dropping tip is required. Harkins and Brown [6] state that any slight flaw in the edge of the capillary may render the effective cross-section of the tube covered by the pendant drop slightly different from the radius as measured by direct observation. In order to avoid any uncertainty in the results from this cause the effective radius was determined directly from the drop weight of very slowly formed drops. If the temperature of the water used is known, the surface tension may be obtained at once from the data of Harkins and Young [5]. Harkins's equation (4) may then be used to determine r when the experimental values of γ and m are inserted therein.

A number of experiments of this nature were performed, the time of formation of a drop being about eight minutes. The resulting values of the tip radius showed good agreement with each other, as the following table indicates.

The radius of the tip will be taken as the average of the above, viz.,

$$r = 0{\cdot}21608 \text{ cm.}$$

This value is used throught the work.

Table I.

Temp. of water.	γ.	m.	r.
20·0° C.	72·75	0·06430	0·21595
24·5° C.	72·04	0·06365	0·21615
22·3° C.	72·37	0·06399	0·21612
24·2° C.	72·07	0·06370	0·21607
24·1° C.	72·09	0·06374	0·21614
24·6° C.	72·02	0·06370	0·21602

Variation of Drop Weight with Rate of Flow.

The rate of flow of water into the drop influences the surface temperature very greatly. For any particular rate of flow, the drop attains a state of equilibrium in which the rate of loss of heat by evaporation just balances the rate of gain of heat from the water flowing into its centre. When the flow is rapid, the fraction of the total mass evaporated from each drop is small and there is little time for surface equilibrium to be established. If, however, the rate of flow is small, considerable evaporation occurs from each drop and the equilibrium surface temperature decreases considerably. On producing rapid evaporation at the surface of one of the very slowly formed drops (8 minutes' period), it was at once obvious that the equilibrium surface temperature was too low to be used in the experiment. The drop surface became rapidly covered with a very thin layer of ice, and finally the whole drop froze solid. The method of formation of this ice was interesting. The surface layer of ice appeared to be forced outward from the drop in the form of a projection, and this projection, once started, grew very rapidly into the form of a long crystal. In the course of one or two seconds this crystal would grow to about 10 cm. in length before the whole drop became solid.

This rapid freezing indicates that the rate of evaporation cannot be determined with very slowly formed drops. On the other hand, if the drops form very rapidly there is not sufficient time for the surface temperature to attain equilibrium before the drop falls. It, therefore, appears that the best rate of flow for these experiments is the slowest at which freezing does not take place. The amount of evaporation from each drop is then as great as possible, so that its measurement is rendered as accurate as possible. In practice the time of formation of drops was usually between 20 secs. and one minute per drop. With these rates of flow the drop increased steadily and evenly in size, and for most of its lifetime appeared to have a fairly constant surface temperature.

The necessity of using rates of flow so great as one or two drops per minute immediately introduced a further difficulty. Harkins's formula (4) refers to a drop formed extremely slowly, and when this condition of very slow formation is violated the formula cannot be applied. Experimentally it appears that the greater the rate of formation the greater the mass of the drop produced. This increase never amounts to more than 1 per cent. or 2 per cent. for very rapid rates of flow, but a correction of this magnitude is of the greatest importance in estimating the surface temperature from the surface tension. It was therefore essential to allow for this variation of drop-weight with rate of flow before proceeding to the estimation of the surface tension.

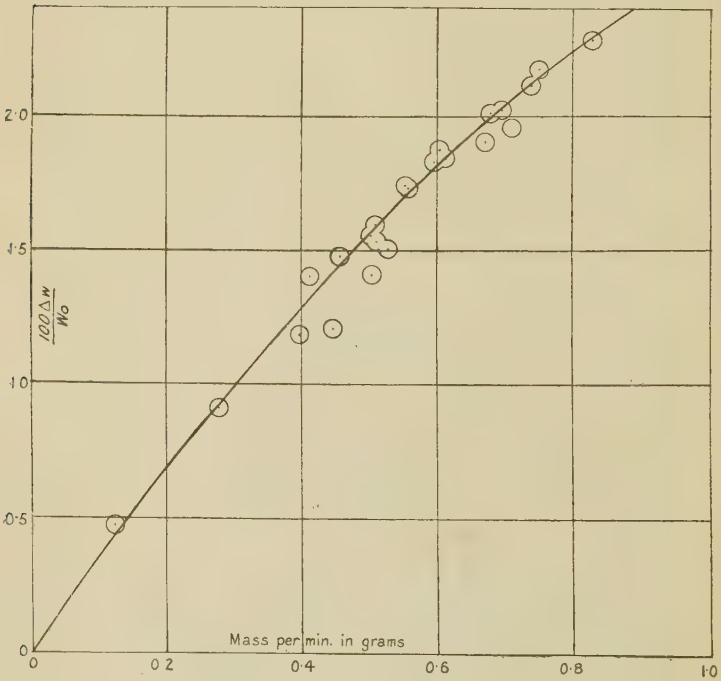
For this purpose a separate set of experiments was performed in which the drop-weight was determined accurately as a function of the rate of flow. This rate was altered by varying the pressure difference between the ends of the thermometer tube H.

Now the drop-weight is altered not only by the rate of flow but also by the temperature of the surface, and in order to maintain the latter constant, evaporation from the hanging drop must be prevented. To prevent such evaporation a quantity of water was placed in the bottom of the container C so as to saturate the space around the drop and also, to minimise the diffusion of vapour throughout the apparatus, the driving pressure was developed by increasing the pressure above the surface of the water in the pipette rather than by diminishing the pressure in C. The experiments were thus conducted with water-saturated air at atmospheric pressure in C and with pressures up to two atmospheres in P. That these precautions were satisfactory was indicated by the fact that the surface tension deduced from the drop-weights of

slowly formed drops at different temperatures agreed very closely with the accepted values corresponding to the temperature of the brass block B.

Since the variation in drop-weight is always small, it was necessary to collect a reasonable number of drops in order to obtain this variation with any accuracy. The number usually collected was from 30 to 50. In every experiment the temperatures of the two ends of the thermometer tube H

Fig. 2.



were measured by means of the thermocouples and the driving pressure was read off the manometer M_1.

The results were represented graphically by plotting the quantity $100\,\Delta w/w$ against the rate of flow. In this expression w is the actual drop-weight when the rate of flow is m gram/min., and $\Delta w(=w-w_0)$ is the difference between the weight and the drop-weight of a very slowly formed drop. The resulting graph is given in fig. 2, whence it

appears that the percentage change is always less than 2·5 the rates of flow used.

This graph may now be used to correct the weights of the drops obtained in the evaporation experiment proper. The increased weight in the latter case is due partly to the reduced surface temperature produced by the evaporation and partly to the rate of flow into the drop. The effect of the velocity of flow may be at once eliminated by the use of the above graph, so that we obtain the true weight of a drop whose surface temperature is the same as that of the actual drop and whose rate of flow is very small. This corrected drop-weight may then be substituted in Harkins's formula at once and so gives the surface tension and the temperature of the actual evaporating drop. It may be added that fig. 2 represents the results of a number of experiments at various temperatures between 10° C. and 25° C. The points arising from the different experiments are indistinguishable, so that the percentage change of weight with rate of flow does not vary appreciably with the temperature of the water used.

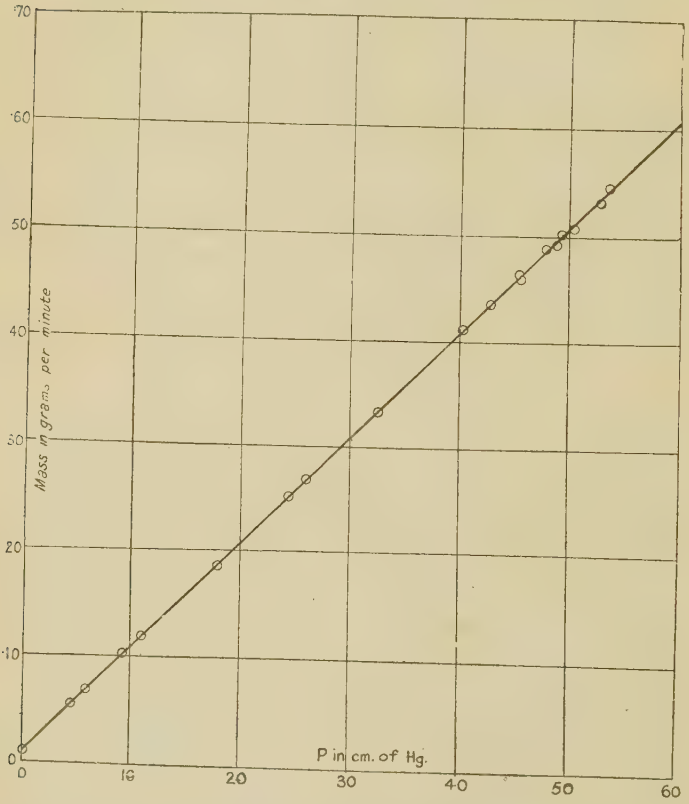
Measurement of Rate of Flow through Capillary.

The mass evaporated from one drop was measured as the difference between the mass of liquid passing through the narrow capillary H during the time of formation of the drop and the mass leaving the capillary tip as a falling drop. This drop-weight is obtained by direct weighing of the fallen drops, and in order to deduce the mass evaporated the rate of flow through the capillary was determined accurately. For this purpose evaporation from the drop was prevented, as described in the last section, and the total time for the formation of a given number of drops (20–30) was measured together with the temperatures at the two ends of the capillary H and the driving pressure on the manometer M_1. The weight of the drops gave the mass emerging per minute at the temperature of the capillary, and hence the mass emerging at a standard temperature of 25·0° C. was deduced. This mass was plotted as in fig. 3, against the driving pressure expressed in centimetres of mercury at 0° C. It appears from the graph that the mass (M) in grams passing through the capillary per minute at a pressure of P cm. of mercury and at a temperature of 25·0° C. is given by the expression

$$M=(9{\cdot}910\,P+9{\cdot}487)\times 10^{-3}\ \text{gram/min.} \quad . \quad . \quad (6)$$

From this expression the mass emerging at any temperature T° C. can be obtained on applying a correction for the change of viscosity. The mass actually evaporating per drop is therefore obtained at once as the difference between that calculated from the above equation and the actual weight of the falling drops. It remains only to measure the average

Fig. 3.



area of the evaporating surface before proceeding to the calculation of the evaporation coefficient f.

Measurement of the Drop Area.

The method employed by Knudsen [1] was used in the determination of the drop area. A series of photographs was taken during the course of formation of the drop, the age of the latter at the instant at which each photograph was

taken being noted. The surface area was calculated graphically from enlargements of the different photographs and the area was plotted against the age of the drop. In the case of mercury, Knudsen [1] found that the area increased almost linearly with the time. For water, however, this was not quite the case, there being a short period in the growth of the drop during which the rate of increase of area diminished. In practice the drop area was not plotted against the age of the surface, but against the mass of the drop. This a little more convenient, as will be seen at once.

If A sq. cm. is the area of the drop at a time t, then it follows from Knudsen's equation (1) that the mass leaving the surface in time dt,

$$= \text{mass entering the surface from the saturated vapour,}$$

$$= 43{\cdot}75 \times 10^{-6} f \mathrm{P} \sqrt{\frac{\mathrm{M}}{\mathrm{T}}} \mathrm{A}\, dt \text{ gram/sec.}$$

Further, if the drop is evaporating into a space whose pressure is p dynes/sq. cm., the net loss of mass in time dt

$$= dm = 43{\cdot}75 \times 10^{-6} f (\mathrm{P} - p) \sqrt{\frac{\mathrm{M}}{\mathrm{T}}} \mathrm{A}\, dt \text{ gram/sec.,}$$

$$= 0{\cdot}2439 f \left(\frac{\mathrm{P} - p}{\sqrt{\mathrm{T}}} \right) \mathrm{A}\, dt \text{ gram/sec.,}$$

if P and p are now measured in mm. of mercury.

Consequently, the total loss of mass during the formation of the drop will be

$$m = 0{\cdot}2349 f \left(\frac{\mathrm{P} - p}{\sqrt{\mathrm{T}}} \right) \int_0^{t_0} \mathrm{A}\, dt,$$

where t_0 is the age in seconds of the surface at the instant at which the drop falls.

Since different experiments were conducted at different rates of flow the relation between A and t differed from time to time It was for this reason that the surface area was plotted against the mass of the drop instead of against the time.

The integral may be written

$$\int_0^{t_0} \mathrm{A}\, dt = \int_0^{m_0} \mathrm{A} \frac{dt}{dm} dm,$$

and since the mass increases linearly with time $\frac{dt}{dm}$ is constant and

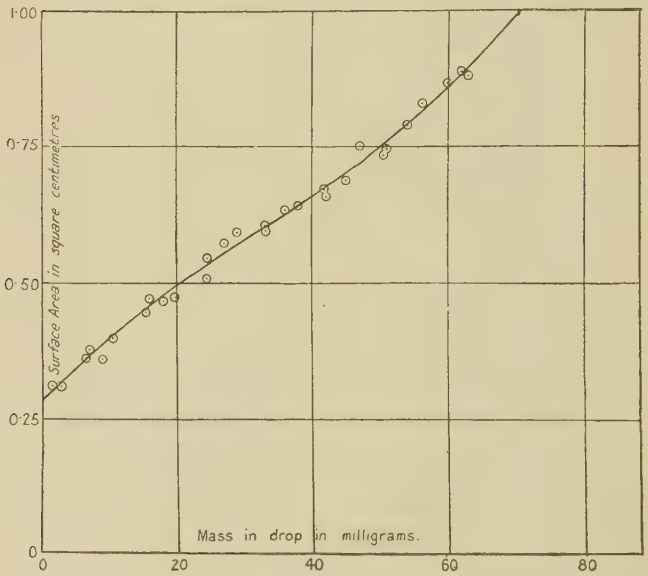
$$\int_0^t A\,dt = \frac{dt}{dm}\int_0^{m_0} A\,dm,$$

where m_0 is the weight of the falling drop.

For the evaluation of this integral an algebraic curve was fitted to the experimental results. The following expression was deduced as the best approximation to these results :

$$A = 0{\cdot}2840 + 13{\cdot}16m - 165{\cdot}4m^2 + 1758m^3 \quad . \quad . \quad (7)$$

Fig. 4.



In fig 4 the circles represent the experimental points while the curve there drawn is obtained from the expression above. This expression is therefore used in the evaluation of $\int A\,dm$, so that

$$\int_0^{t_0} A\,dt = \frac{dt}{dm}\int_0^{m_0} A\,dm,$$

$$= \frac{dt}{dm}\{0{\cdot}2840m_0 + 6{\cdot}580m_0^2 - 55{\cdot}13m_0^3 + 439{\cdot}5m_0^4\}. \quad (8)$$

As before, m_0 is the weight of the *falling* drop.

Finally, we have

$$m = 0{\cdot}2439\left(\frac{P-p}{\sqrt{T}}\right) f \frac{dt}{dm}\{0{\cdot}2840 m_0 + 6{\cdot}580 m_0^2 - 55{\cdot}13 m_0^3 + 439{\cdot}5 m_0^4\} \quad . \quad (9)$$

as the expression for the mass in grams evaporated during the formation of one drop. All the quantities occurring in (9) can be determined, with the exception of f. T, the surface temperature, follows at once from the surface tension of the evaporating drop. P is the saturated-vapour pressure at the temperature T° C., m_0 is the drop-weight, and dt/dm is determined from the rate of flow of the water into the drop. A comparison of m as determined from equation (9) with the experimentally determined mass evaporating from one drop then gives the evaporation coefficient f.

Measurement of evaporation coefficient.

In the experiments for the actual measurement of the evaporation coefficient the pipette was filled up to a standard level with air-free distilled water and the whole apparatus was slowly evacuated until the pressure inside was only a few centimetres of mercury. The tap W was then closed and clean air admitted through the tap Y until the requisite driving pressure was obtained. The container C was then connected through a wide glass tube to the high-speed vacuum pump, so that the pressure around the evaporating drop rapidly fell to an equilibrium value of 1 mm.–2 mm. The falling drops were collected in one of the small vessels V, and the manometer M_2 was observed continuously until the meniscus appeared quite steady in the reading telescope. The positions of the small vessels V were then interchanged by rotation of the container C and a counted number of drops were collected. At the same time the total time required for the formation of the drops was noted so that the rate of flow could be calculated later. The temperature of the thermometer tube H was also taken immediately before and after the collection of the drops. A second observer meanwhile noted the pressure variation on the manometer M_2. It was found that if no water were present in the container C (except the hanging drop, of course) the pressure inside was constant to within 0·02 mm. Whenever a drop fell this pressure increased slightly, but returned to its original value within one or two seconds. This increase was probably due to evaporation from the newly-formed surface after the falling of the previous drop. The fact that the pressure returns

to its original value so rapidly is taken to indicate that the newly-formed surface rapidly attains temperature equilibrium. At the conclusion of the experiment the stop-cock Z was closed, so that the pressure of the experiment was maintained in the manometer and could be measured at leisure. Air was then readmitted to the apparatus, the container C was removed, and the weight of the collected drops obtained. The pressure was not kept below the saturated-vapour pressure for periods longer than were necessary, thus avoiding, so far as possible, the loss of the experiment through explosive boiling of the collected drops.

The following is a typical example of the results obtained and illustrates the method adopted for the calculation of f:—

Experimental Results.

Drop-weight *in vacuo* = 0·06895 gram.
Rate of flow through thermometer tube = 0·2484 gram/min.
∴ Correction for rate of flow = 0·84 per cent. (from fig. 2).
Corrected drop-weight = 0·068375 gram.
∴ Surface temperature = −7·73° C.
and P = saturated-vapour pressure at this temperature = 2·567 mm.
p = pressure in container C = 1·735 mm.
∴ $(P-p) = (2{\cdot}567-1{\cdot}735) = 0{\cdot}832$ mm., and T = 265·3° A.

$$\int_0^{t_0} A\,dt = 10{\cdot}30 \text{ sq. cm.–sec.}$$

Therefore mass evaporating according to theory.

$$0{\cdot}2439\left(\frac{P-p}{\sqrt{T}}\right)\int_0^{t_0} A\,dt \text{ gram/drop} = 0{\cdot}1283 \text{ gram/drop.}$$

Now the driving pressure = 25·65 cm. at 0° C.
∴ Mass passing through capillary at 25·0° C. = 0·26369 gram/min. (by equation 6).
Average temperature of capillary = 25·35° C.
∴ Mass passing through capillary at this temperature = 0·26584 gram/min.
Time of formation of one drop = 16·64 sec.
∴ Mass entering drop during its formation = 0·073726 gram.
Mass leaving in liquid form = 0·06895 gram.
∴ Mass evaporating = 0·004776 gram.

Therefore $$f = \frac{4776}{128300} = 0{\cdot}037$$

or, the experimental rate of evaporation is only 3·7 per cent. of that predicted by Knudsen's equation.

It should be noted that in the experiments for the determination of f the drops are formed in a vacuum, while they are weighed in air. A buoyancy correction is therefore required. In the earlier experiments on the variation of drop-weight with rate of flow no such correction was necessary.

TABLE II.

Pressure in apparatus (p). mm.	Saturated-vapour pressure (P). mm.	(P$-p$). mm.
1·780	2·940	1·160
1·735	2·567	0·832
1·800	2·810	1·010
1·700	2·643	0·943
1·760	2·610	0·850
1·720	2·500	0·780
2·005	2·843	0·838
2·014	2·715	0·701
2·527	3·009	0·482
4·709	5·052	0·343
4·010	4·250	0·240
5·221	5·540	0·319
4·447	4·736	0·289
11·520	11·652	0·132
11·260	11·430	0·170
13·750	13·750	too small to measure.

It will be seen from equation (9) that the possibility of carrying out an experiment at a pressure below the saturated-vapour pressure corresponding to the temperature of the surface depends directly on the value of the evaporation coefficient f. If this constant is unity, as for other substances, then for (9) to agree with the experimental results the value of (P$-p$) in the equation must be very small, and it should be impossible to distinguish between P and p except at very low pressures (say below 1 mm.). It is, therefore, of interest to examine the value of this pressure difference as determined experimentally as a function of the working pressure, and this is done in Table II.

It is seen that there is a very distinct difference between the values of P and p and that, as would be expected, $(P-p)$ diminishes rapidly with increasing p. For this reason the most reliable values of f will be those deduced from experiments in which the value of p was small. Since f depends directly on $(P-p)$ it becomes somewhat indeterminate when this quantity is too small. Hence most of the experiments were performed with fairly slow rates of flow, rapid evaporation, and low pressure in the container C.

Table III.

Uncorrected drop-weight.	Correction.	Corrected drop-weight.	Pressure in apparatus.	f.
grams.	per cent.	grams.	mm.	
0·06863	0·860	0·06804	1·780	0·0289
0·06895	0·840	0·06837	1·735	0·0372
0·06873	0·865	0·06814	1·800	0·0353
0·06885	0·835	0·06828	1·700	0·0299
0·06888	0·820	0·06832	1·760	0·0385
0·06900	0·820	0·06844	1·720	0·0366
0·06873	0·900	0·06812	2·005	0·0437
0·06857	0·850	0·06799	2·527	0·0489
0·06878	0·825	0·06822	2·014	0·0415
0·06745	0·765	0·06694	4·709	0·0422
0·06771	0·635	0·06728	4·010	0·0584
0·06712	0·545	0·06676	5·221	0·0315
0·06727	0·300	0·06707	4·447	0·0268

The fact that the difference between P and p can be detected up to pressures of about 10 mm. therefore indicates that the value of f must be considerably less than unity.

The results of a number of determinations of f are collected in Table III., whence it will be seen that the average value of this constant is about 0·04.

As was anticipated, the values of f are more consistent the lower the pressure at which the experiment is conducted.

In the earlier work of Alty and Nicoll (*loc. cit.*) the value of f was found to increase steadily and rapidly with decrease of pressure from an extremely small value up to a value of 0·015 for zero pressure. It was therefore intended in the present work to plot the resulting values of f against the

pressure and obtain, by extrapolation, the value corresponding to evaporation into a vacuum. The results, however, show that f is independent of pressure to within the error of experiment, and the true value is taken as the mean of those obtained from experiments performed at pressures below 5 mm., viz. :,

$$f = 0{\cdot}038 = 0{\cdot}04 \text{ (approx.)}.$$

The variation of f with p in the earlier work was undoubtedly due to the error in the thermocouple measurement of the surface temperature. The constancy of f in the present determination might be taken as an indication that the actual surface temperature has been measured.

In the above determination of f it is assumed that the surface-temperature equilibrium is attained very quickly and that all the evaporation takes place at the temperature

TABLE IV.

Pressure p.	Surface temperature.	Temperature difference.
mm.		
1·72	−7·45° C.	32·45° C.
2·11	−6·55° C.	31·55° C.
5·31	2·25° C.	22·75° C.
9·83	11·35° C.	13·65° C.
14·95	17·35° C.	7·65° C.
23·51	25·00° C.	0·00° C.

deduced from the drop-weight. This assumption is supported by the fact that after one or two seconds the pressure around the drop does not vary appreciably. However, if this assumption is not strictly true and the drop surface temperature requires some seconds to decrease from 25° C. to its final value, this cannot explain the small value of f. An effect of this nature would materially increase the *experimental* rate of evaporation, and so would increase the value of f as deduced from the experiment. Consequently, if it is necessary to correct the results here given for an effect of this nature, the final value of f would be *smaller* than those given in the above table.

The temperature difference between the surface and the mass of the liquid will also vary with the rate of evaporation, *i. e.*, with the pressure p. The rapid increase in this difference of temperature with decrease of p is shown in Table IV. and fig. 5.

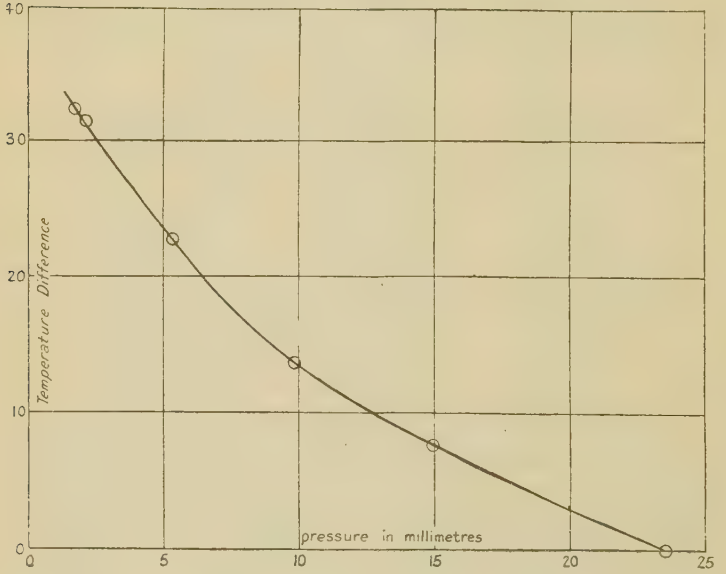
Summary.

The maximum rate of evaporation of water at temperatures between $+4°$ C. and $-8°$ C. has been measured and has been shown to be only a small fraction of that deduced from the Knudsen equation. The value of the evaporation coefficient f, which is defined as the ratio of the experimental to the theoretical rates of evaporation, is

$$f = 0{\cdot}04.$$

I wish to take this opportunity of expressing my sincere thanks to Dr. E. L. Harrington and Dr. C. A. Mackay for

Fig. 5.



their very kind help on many occasions when the work required the attention of two persons. I must also thank Mr. A. H. Cox, instrument maker in the department, for his assistance.

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(7) Alty, T., 'Nature,' p. 167 (July 30th, 1932).

University of Saskatchewan,
Saskatoon, Canada.
July 11th, 1932.

XI. *On the Nature of the Dark Modification of Active Nitrogen.* *By* Prof. J. Okubo *and* H. Hamada*. (From the Laboratory of Physics, Sendai, Japan.)

[Plate V.]

§ 1. *Introduction.*

IT has already been reported by Cario and Kaplan † that the visible afterglow of active nitrogen is extinguished when it is heated to high temperature, and it has been shown that the glowless state is capable of exciting only the D-line, but not the other lines of sodium. Willey ‡ has also found that active nitrogen changes to glowless form on passing through it a weak electric discharge, and he has confirmed the fact that in this non-glowing state it still remains chemically active. According to the theory put forward by Cario and Kaplan, the visible afterglow of active nitrogen results from collisions of the second kind between the metastable molecules in the $A^3\Sigma^{(0)}$ (8·2 volts) state and the metastable atoms in the ^2D state (2·37 volts), or in the ^2P state (3·56 volts), existing in the active nitrogen, and by heating or passing a weak electric discharge through it the metastable molecules disappear, while the metastable atoms remain unchanged, and the glowless state is still active, though the characteristic afterglow is not observed. Cario and Kaplan have pointed out the existence of this glowless state as one of the evidences powerfully supporting their view of the nature of active nitrogen. However, there remain some questions with regard to the existence of this glowless state, namely

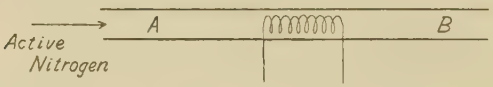
* Communicated by the Authors.
† G. Cario and J. Kaplan, *Zeits. f. Phys.* lviii. p. 769 (1929).
‡ E. J. B. Willey, Journ. Chem. Soc. Lond. p. 2831 (1927); etc.

whether it is quite different from the after-glowing state as Cario and Kaplan consider, and whether the glowless state observed by these scientists is quite the same in its nature as that observed by Willey or not ? This paper is a report of the results of the experiments which were carried out in order to solve the above mentioned questions.

§ 2. *On the catalytic actions of Metals and Glass surfaces on Active Nitrogen.*

Before observing the dark modification formed by heating active nitrogen, it is necessary to study the catalytic actions of metals and glass surfaces on active nitrogen. For the purpose of observing the effect of metals, a small coil of aluminium wire was inserted in the afterglow tube (fig. 1). The total length and the diameter of the wire used was about 30 cm. and 0·05 mm.

Fig. 1.



respectively, and it was inserted in the Wheatstone bridge so as to form one arm of it. By measuring the variations of the electrical resistance of the wire when active nitrogen flows through the tube, the rises of temperature of the wire can be calculated, by doing which it is possible to compare the magnitudes of the catalytic action of the wire.

In the case where the active nitrogen derived from pure nitrogen and that derived from nitrogen slightly contaminated with oxygen (about 3 per cent.) flows through the tube, it was found that the after-glow does not visually change at the position before (A) and after (B) when the gas passes through the coil, but that the temperature of the wire rises considerably in the latter case compared with the former. On observing the afterglow at positions A and B with a quartz spectrograph, the spectra at the two positions in the case of pure nitrogen do not show any difference, while in the case of impure nitrogen the β and the γ bands appear more enhanced at position B than at A. In the case

where the active nitrogen is derived from a source that is contaminated with greater contents of oxygen (about 5 per cent. or more), the coil is heated to a much higher degree, and the after-glow changes colour from a yellow to a blue tint after the active gas has passed through the coil; the spectrographic observations show that the α-bands are extinguished while bands β and γ are considerably enhanced.

Similar phenomena are also observable in the case of active nitrogen flowing through a heated portion of the glass tube. In the case where pure active nitrogen flows through a heated portion, at about 650° C., of a long tube of Pyrex glass, it was found that the intensity of the visible after-glow much decreases, but is not destroyed at the heated portion, being accompanied by a modification of the intensity distribution in the α-bands, while a little enhancement of the β as well as the γ-bands relative to the α-bands was observed at this portion. No great difference in the total intensity or in the intensity distribution of the spectrum was observed between the after-glows at the positions before and after the active gas had passed through the heated portion. In this experiment, the diameter of the tube was 1 cm. and the length of the heated portion was about 30 cm.

In the case where active nitrogen contaminated with oxygen (3 per cent.) flows through the tube in the same condition as in the above case, the effects are not the same. The visible after-glow appears very weak at the heated portion and is completely extinguished there, when the flowing active nitrogen is sufficiently contaminated (5 per cent. or more). The spectrographic observations also show that bands β and γ appear more enhanced and the α-bands are extremely weak at the heated portion. After the active nitrogen had passed through the heated portion relative enhancements of the β and γ-bands to the α-bands are observed in comparison with their relations in the portion before the heated position, the total intensity of the visible glow decreases, and, in the case in which a sufficiently contaminated active nitrogen flows, all the bands almost completely disappear on leaving the heated portion.

From the above experiments, it will be concluded that the heated surface of Pyrex glass wall has no

appreciable effect on pure active nitrogen, but in the case of impure active nitrogen, the heated glass surface or the high temperature itself together with the oxygen contained in the nitrogen acts so as to extinguish the visible after-glow of the active nitrogen. Therefore, in order to study the effect of heating on the visible after-glow, it is absolutely necessary to use nitrogen which is free from oxygen.

The catalytic effect of the walls of a Pyrex glass tube, cooled after heating the tube at about 650° C. for over 100 hours, the active nitrogen flowing continually through it, was also observed. Herzberg * has already reported that the clean surface of the glass wall acts catalytically in the re-combinations of atoms into molecules, but it seems that the catalytic action in this case is not the same as in his case, and the effect is perhaps due to some compound formed on the surface of the glass, because this surface emits a green fluorescence and loses its action after being washed with nitric acid or with sulphuric acid mixed with potassium bichromate and distilled water. But on leaving the tube for over three days after filling it with air or hydrogen gas no change is observed.

§ 3. *On the after-glow of Active Nitrogen at high temperatures.*

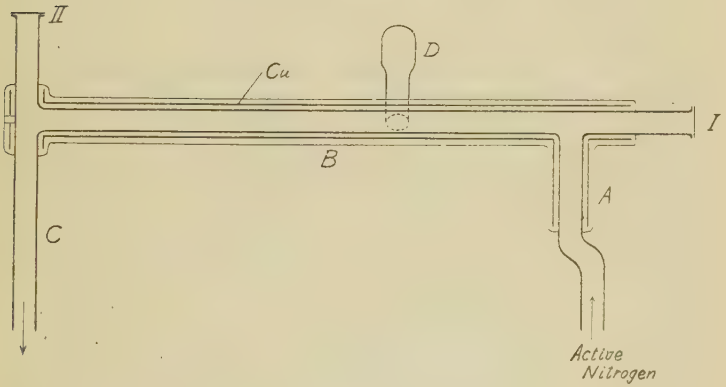
It has been reported by Cario and Kaplan, Willey, and others that the visible after-glow of active nitrogen is extinguished in cases where it was heated, or where a weak electric discharge had been passed through it; it is very important to study whether the dark modifications formed in these two cases are quite the same in nature or not. For the purpose of solving this problem, the following experiments have been carried out. It is also to be remarked that great care must be taken in regard to the purity of the gas, as the impurities, especially small contents of oxygen, produce a considerable effect on the after-glow of the active nitrogen, as shown in the preceding paragraph.

First, spectrographic observations of the visible after-glow at and beyond the heated portion of the tube, through which the pure active nitrogen flows, were carried

* G. Herzberg, *Zeits. f. Phys.* xlvi. p. 878 (1928).

out. The tube used was made of Pyrex glass, 1 cm. in inner diameter, and around a portion, 30 cm. in length of it, (hereafter it will be denoted as portion B), was wrapped a thin sheet of asbestos and of copper and over this was again covered with a sheet of asbestos (fig. 2). In order to heat this portion intensely seven Bunsen burners were used and it was ensured that the temperature at every point of this portion was nearly the same. The light emitted at this heated portion was observed through a quartz window I. A side tube A was attached to the tube B and it was covered along its length (about 5 cm.) in the same manner as the portion B. This tube

Fig. 2.



serves for cutting off the light emitted by the active nitrogen before it is sufficiently heated. Another side tube C was also attached to the portion B for the purpose of observing, through a quartz window II, the light emitted after the active nitrogen had passed through the heated portion B. The tube is also very helpful in watching over the purity of the gas, as the intensity of the after-glow is reduced after passing through the heated portion in the case of the impure active nitrogen used as described in the preceding paragraph.

In the heated conditions the α-bands appear, as a whole, much less intense than at room temperature, as above stated, and from the reproductions of the spectrograms together with the photometric curves obtained in the case where the tube B is heated at 600–650° C. (Pl. V. *a*)

and at the room temperature (Pl. IV. *b*), it will be seen that the relative reduction of the intensity is the greatest for the green group and least for the red and that the distribution of the intensity of this band system, as a whole, changes, and the group in the longer wave-lengths becomes relatively intense. A close examination of the distribution of every band in each group shows also a displacement of the intensity maximum towards the longer wave-lengths, *i. e.* the intensities of the bands with $v' = 10$ or less and $v' = 5$ or less are enhanced relatively to the bands with $v' = 11$ and $v' = 6$ or 7, respectively, and the maxima at the bands with $v' = 11$ and $v' = 6$ which appear most intense in the spectrograms at room temperature, tend to displace towards the bands with $v' = 10$ and $v' = 5$. The modifications of intensity of the α-bands of active nitrogen cooled by liquid air had already been observed by Herzberg * and also by Cario and Kaplan †, it was shown that the maximum of intensity in every group of the α-bands is displaced at these lower temperatures in the direction of the shorter wave-lengths. The results obtained in this experiment are well in accordance with those obtained by these scientists, and it is certain that the bands corresponding to the less excitational energies are more enhanced at high temperature.

Next, the modifications of the intensities of the β and the γ-bands are observed. The bands appear very weak in the case where pure nitrogen is used, and the reductions of their intensities at high temperatures are less, compared with that of the α-bands. In the case of impure active nitrogen, these bands appear more intense in the heated portion than the α-bands and it was confirmed that the greater the enhancemnt of the β and γ-bands, and the more completely the α-bands were observed to fade at a high temperature, the more impure was the nitrogen used.

In order to confirm Cario and Kaplan's theory regarding the nature of active nitrogen, it is very desirable to observe the metallic spectra, especially those of sodium and mercury, when excited by the dark modification produced by heating the active nitrogen. For this

* G. Herzberg, *Zeits. f. Phys.* xlix. p. 512 (1928).
† Cario and J. Kaplan, *loc. cit.*

purpose, we obtained the spectrogram of the light emitted in portion B, in which a very small quantity of the vapour of sodium or mercury, evaporated from the side tube D, was excited by the dark modification, *i. e.* weakly-glowing pure, or nearly glowless impure active nitrogen at a temperature of 600°–650° C. (fig. 2). The spectrograms obtained were exactly the same as those obtained in the case of excitation by ordinary non-heated active nitrogen, and the highest level of energy excited was that of 9·51 volts exactly, neither more nor less. Also on comparing the photometric curves of the spectrograms with those obtained in the condition when the active nitrogen was not heated, exactly the same distribution of intensity among the appearing lines was observed. In comparing our results with theirs it must be noted that Cario and Kaplan observed the D-line only in the case of sodium. Similar results to those in the case of pure active nitrogen are also obtained when using slightly contaminated nitrogen. On the other hand, in the case where an active nitrogen is derived from very impure sources it was found that the gas becomes perfectly glowless when heated, and it is neither possible to excite the D-line, nor to detect the activity with a sensitive thermopile in the portion C.

Using active nitrogen of the same purity, it was also confirmed that the intensity of the visible after-glow (α-bands) heated to 600°–650° C. is decreased to about one-fortieth of that at room temperature, while the intensity of the D-line excited by the active nitrogen heated to the former temperature is decreased to about one-seventh of that directly excited by the non-heated active nitrogen. Though it is very difficult to ensure that all the conditions of the experiments are invariably the same in these two cases and therefore these numerical values have no quantitative meaning, it may be fairly stated that by heating the active nitrogen at a constant pressure the intensity of the sodium spectrum resulting from the triple collisions between metallic atoms and active nitrogen is not so much decreased as the intensity of the visible after-glow itself.

It is certain that the energy of active nitrogen is the same in the heated state as in the ordinary glowing state, and therefore the so-called dark modification is not such a modified form of active nitrogen as Cario

and Kaplan have conjectured, but as regards the energy it is the same as the ordinary after-glowing form, though the intensity of the glow is markedly diminished by the heating. It seems very proper to consider that the visible after-glow of active nitrogen is excited as a by-process of the re-combinations of nitrogen atoms indirectly, and therefore it is emitted in ordinary cases but not always so. From the fact that even when such a small quantity of the sodium vapour is mixed with active nitrogen that its pressure only amounts to 1/1000 mm. the yellow glow of sodium is very distinctly observable, while the α-bands in that glow become very faint, it will be inferred on a comparison of the two, viz. the visible after-glow and the spectrum of metallic vapour as regards the probability of their being excited, that the excitation of the first-mentioned is less probable. Perhaps there will be required two stepped excitations for the visible α-bands and a one stepped excitation for the metallic spectra. Therefore, assuming only that the excitation probability of the visible after-glow (α-bands) is much more reduced with the rise of temperature, it will be easily understood that active nitrogen has the same content of energy and excites the metallic spectra, independent of the intensity of the visible after-glow.

From the above results it seems that some modifications are needed in Cario and Kaplan's theory regarding the visible after-glow of active nitrogen. They considered that the visible after-glow is emitted as the result of the collisions of the second kind between the metastable molecules in the A (8·2 volts) level and the metastable atoms in the ^{2}D and ^{2}P levels. It is just as comprehensible that the bands, which correspond to the vibrational quantum numbers $v' = 6$ or 7 and 12, are selectively enhanced in the after-glow at a low temperature, since the energies of the excitation of these bands are nearly equal to the sums of the energies of the metastable molecule and of the metastable atoms, and in this condition their kinetic energies are small, their effect being only very slight. However, on this assumption, it seems very difficult to account for the fact that the maximum of intensity in the band system or in the band group, is displaced in the direction of the longer wave-lengths when the temperature of the active

nitrogen rises, for owing to this circumstance the kinetic energies of the colliding molecules and atoms as well as the vibrational energy of the former will become greater, and they will exert a considerable influence on the energy transference during the collisions. It may therefore be expected that the maximum of intensity of the band system or of the group will be displaced in the direction of the shorter wave-lengths whereas the results found by observation do not confirm this belief.

Again, it will also be very difficult to suppose that the displacement is due to the temperature effect on the molecules excited in the $B^3\Pi$ state, as the life of the excited molecule in this state is not so long, and also because the frequency of the collisions taking place during the life of the excited molecule with other molecules and atoms is greater at lower than at higher temperatures, under the same condition of pressure, and the transitions of the states of higher vibrational energies to those of lower ones are more probable than the reverse processes. Therefore the maximum of intensity in the band system as well as in each group will be displaced in the direction of the longer wave-lengths at the lower temperature in spite of the conflicting results of observation.

As described above, we unfortunately were unable to discover the so-called dark modification, the existence of which Cario and Kaplan have pointed out, but we have confirmed the fact that active nitrogen possesses the same energy even in a strongly heated state—weakly glowing or nearly dark according to its purity—as in the ordinary glowing state ; it seems, therefore, that some modification is needed in Cario and Kaplan's theory of the nature of active nitrogen.

§ 4. *The nature of Willey's dark modification of Active Nitrogen.*

Willey has already reported that when a weak electric discharge passes through it the visible after-glow of active nitrogen is extinguished in spite of the persistence of its chemical activity. It will be very interesting to discover whether this glowless state of nitrogen has the same nature as that which has been found by heating and discussed by Cario and Kaplan or not. It is clearly observable that, in contradiction to Cario and Kaplan's

dark modification, which recovers the after-glow after the gas has passed through the heated portion, Willey's glowless state never recovers its glow, and it will be shown that the former is quite distinct from the latter. Consequently, for the purpose of examining the activity of Willey's glowless state, a long straight glass tube 1·5 metres in length and 1·5 cm. in diameter was connected directly with the after-glow tube, in which the second electric discharge is carried out. The outer surface of this tube was wrapped up in black cloth, and the tube was thus completely screened from any stray light. On passing active nitrogen—which had been subjected to a second weak electric discharge in the after-glow tube—through this long tube, and by looking carefully through the tube placed end-on to the view, it was possible to confirm the presence of a very minute quantity of glowing active nitrogen. As a sensitive means of detecting the activity of any glowless state, a modified form of a thermopile of Moll's type was adopted. This thermopile was prepared by a workman of this laboratory, and consisted of ten junctions of narrow thin strips of constantan and manganin, and was so arranged that all the junctions lie on one and the same straight line in a plane. It was coated with a thin layer of copper oxide along the line of junctions and of shellac on the remaining part of the thermopile. This thermopile has a sensibility for the radiations about seven times that usually found in Moll's microphotometer.

On passing both the glowing and the glowless nitrogen in turn over this thermopile which was placed in the tube, and observing the deflexions of the mirror of the galvanometer connected with the thermopile, the following results caused by the activity of the gas were observed ; (1) the glowing nitrogen, even when its concentration is extremely minute, acts perceptibly on the thermopile, and the greater the deflexions of the mirror, the more intense is the after-glow observed in the long tube above-mentioned, *i. e.* the deflexion is always directly proportional to the intensity of the visible after-glow (2) the glowless nitrogen produced by the second weak electric discharge through pure active nitrogen does not generate electro-motive force in the couple (of course it cannot excite the sodium D-line), (3) in the case of the glowless nitrogen produced by a weak discharge through

considerably contaminated active nitrogen, the mirror is considerably deflected as if the glowless gas retained its activity, when the gas was very rapidly streaming through the tube, or when the thermopile was placed very near the electrode of the second discharge. However it is easily confirmed that the deflexion is certainly due to the invisible after-glow from β and γ-bands or to some other impurity, but not to the pure nitrogen at all. Although the above observations are merely qualitative, it will be sufficient to show that the active nitrogen loses activity simultaneously with the quenching of the visible after-glow by a weak electric discharge and, in disproof of Willey's results, the existence of the glowless state was not confirmed.

XII. *Whirling of a Journal in a Sleeve Bearing.*

By David Robertson, *D.Sc., M.I.E.E.**

I. *Introduction.*

THE theory of film lubrication, based on the work of Osborne Reynolds[1]† and Sommerfeld[2], has for the most part been applied to the steady state of equilibrium; the motion of the journal when disturbed from that position of equilibrium has received somewhat less attention.

Newkirk and Taylor[4] have described model experiments which they carried out to elucidate certain vibration troubles encountered with high speed machines, and Hummel[6] has also given experimental results in support of his theoretical deductions.

On the theoretical side, Harrison[3] has dealt with the sleeve bearing, and Newkirk and Taylor have given a rough theory which partly explains the phenomena they observed. Hummel has published an elaborate, but approximate, mathematical treatment for the case of a rigid rotor supported in semi-cylindrical bearings, based in part on the earlier work of Stodola[5].

Unfortunately, Harrison has made a slip at the very beginning of his paper, by omitting to allow for the movement of the journal centre when estimating the tangential

* Communicated by the Author.

† The numbers refer to the Bibliography at the end.

component of the surface velocity ; that slip by itself invalidates the whole of his subsequent deductions, but at a later stage he also assumes that the rotor has no inertia.

The present paper is confined to the sleeve bearing, and considers both rigid and elastic rotors. The more important pad bearing could be dealt with on somewhat similar lines, but the mathematical expressions required are decidedly cumbersome.

2. *List of Symbols.*

r = radius of journal.
δ = radial clearance of bearing.
h = thickness of film at point under consideration.
θ = position angle for that point.
e = eccentricity of journal centre in bearing.
a = e/δ.
ω = angular velocity of shaft, referred to as its "rotation."
ω_e = that of the eccentricity.
ω_0 = critical angular speed of elastic rotor.
λ = viscosity of oil.
p = oil pressure at point under consideration.
q = tangential stress on surface of journal at a given point.
Q = volume of flow of oil past section considered.
Q_0 = that part of Q which does not vary with the position.
x = distance measured forwards along the tangent to the journal.
y = distance measured radially outwards from the journal surface.
dx = $r\,d\theta$.
U = tangential component of velocity of journal surface.
V = radial component of same.
u = component of velocity of oil in the x-direction.
v = that in the y-direction.
I = $(1-a\cos\theta)^{-1}$.
J_n = $aI^n \sin\theta$.
J_0 = $(1-a^2)^{-\frac{1}{2}} \sin^{-1}\{(1-a^2)^{\frac{1}{2}} I \sin\theta\}$.
j = "90° ahead of."
F_{np} = component normal to eccentricity of force due to oil pressure.
F_{ep} = component of same along eccentricity.
κ^2 = F_{np}/δ.

F_{nf} = component normal to eccentricity of force due to frictional drag.

F_{ef} = component of same along eccentricity.

Fe = elastic force on journal due to deflexion of shaft.

g = acceleration due to gravity.

M = mass of rotor.

ρ = radius of rotor whirl at critical speed.

2α = frictional constant for rotor whirl.

3. *Integrals Required.*

It will facilitate the work if we first set down the integrals required, which involve some rather interesting functions. Let

$$I = (1+a\cos\theta)^{-1}, \quad . \quad . \quad . \quad . \quad . \quad (3.01)$$

$$aI\cos\theta = 1-I, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.02)$$

$$aI^n\cos\theta = I^{n-1}-I^n, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.03)$$

$$a^2I^2\sin^2\theta = -1+2I-(1-a^2)I^2, \quad . \quad . \quad . \quad (3.04)$$

$$a^2I^n\sin^2\theta = -I^{n-2}+2I^{n-1}-(1-a^2)I^n. \quad . \quad (3.05)$$

Also let

$$J_0 = (1-a^2)^{-\frac{1}{2}}\sin^{-1}\{(1-a^2)^{\frac{1}{2}}I\sin\theta\}, \quad . \quad . \quad (3.06)$$

$$J_1 = aI\sin\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.07)$$

$$J_n = aI^n\sin\theta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.08)$$

Then

$$dI/d\theta = aI^2\sin\theta = J_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.09)$$

$$dI^n/d\theta = naI^{n+1}\sin\theta = nJ_{n+1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.10)$$

$$\int J_n\,d\theta = I^{n-1}/(n-1), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.11)$$

$$\int J_1\,d\theta = \log I, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.12)$$

$$dJ_0/d\theta = \{aI^2\sin^2\theta+I\cos\theta\} \div \{1-(1-a^2)I^2\sin^2\theta\}^{\frac{1}{2}} \quad . \quad . \quad . \quad (3.13)$$

$$= \frac{\{-1+2I-(1-a^2)I^2+1-I\}}{[a^2-(1-a^2)\{-1+2I-(1-a^2)I^2\}]^{\frac{1}{2}}} \quad . \quad (3.14)$$

$$= \{I-(1-a^2)I^2\} \div \{1-2(1-a^2)I+(1-a^2)^2I^2\}^{\frac{1}{2}} \quad . \quad . \quad . \quad (3.15)$$

$$= I, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.16)$$

$$\int \mathrm{I}\, d\theta = \mathrm{J}_0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.17)$$

$$d\mathrm{J}_n/d\theta = na^2\mathrm{I}^{n+1}\sin^2\theta + a\mathrm{I}^n\cos\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.18)$$

$$= -n\mathrm{I}^{n-1} + 2n\mathrm{I}^n - n(1-a^2)\mathrm{I}^{n+1} + \mathrm{I}^{n-1} - \mathrm{I}^n. \quad (3.19)$$

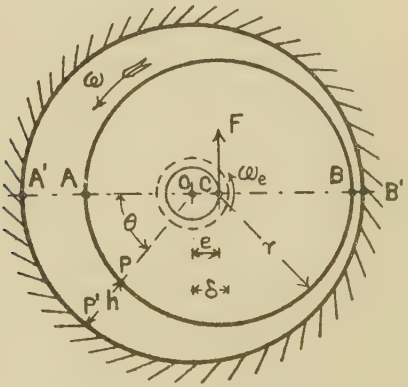
$$= -(n-1)\mathrm{I}^{n-1} + (2n-1)\mathrm{I}^n - n(1-a^2)\mathrm{I}^{n+1}, \quad (3.20)$$

$$(n-1)(1-a^2)\int \mathrm{I}^n\, d\theta$$

$$= -(n-2)\int \mathrm{I}^{n-2}\, d\theta + (2n-3)\int \mathrm{I}^{n-1}\, d\theta - \mathrm{J}_{n-1}. \quad . \quad . \quad . \quad (3.21)$$

The method here followed differs somewhat from that of Sommerfeld. In the first place, we prefer to have the numeric a proportional to the eccentricity, which it has to represent in the dimensionless equations, rather than pro-

Fig. 1.



Journal in sleeve bearing.

portional to its reciprocal. Because he makes the other choice, his function is $(a+\cos\theta)^{-1}$ instead of our I. Further, his $\mathrm{J}_n = \int (a+\cos\theta)^n\, d\theta$, whereas our J's are the simpler elements of which the corresponding integrals are built up. As may be seen above, the introduction of the symbol I greatly simplifies the transformations required in evaluating the various integrals.

The expressions for these integrals for the particular values of n which are required in the following treatment are given in the Table, as well as their numerical values when taken between the limits of 0 and 2π.

4. *Force on Journal due to Oil Pressure.*

In the diagram, where the clearances are greatly exaggerated, O is the centre of the bearing, C that of the journal,

Table of Integrals required.

Function.	Integral.	$\int_0^{2\pi}$.
$I=(1+a\cos\theta)^{-1}$	$J_0=(1-a^2)^{-\frac{1}{2}}\sin^{-1}\{(1-a^2)^{1/2}I\sin\theta\}$	$2\pi/(1-a^2)^{1/2}$
I^2	$(J_0-J_1)/(1-a^2)$	$2\pi/(1-a^2)^{3/2}$
I^3	$\{(2+a^2)J_0-3J_1-(1-a^2)J_2\}\div 2(1-a^2)^2$	$\pi(2+a^2)/(1-a^2)^{5/2}$
$aI\sin\theta=J_1$	$\log I$	0
$aI^2\sin\theta=J_2$	I	0
$aI^3\sin\theta=J_3$	$\frac{1}{2}I^2$	0
$aI\cos\theta$	$\theta-J_0$	$-2\pi\{1-(1-a^2)^{1/2}\}/(1-a^2)^{1/2}$
$aI^2\cos\theta$	$(-a^2J_0+J_1)/(1-a^2)$	$-2\pi a^2/(1-a^2)^{3/2}$
$aI^3\cos\theta$	$\{-3a^2J_0+(1+2a^2)J_1+(1-a^2)J_2\}\div 2(1-a^2)^2$	$-3\pi a^2/(1-a^2)^{5/2}$
$a^2I\sin^2\theta=aJ_1\sin\theta$	$\theta-a\sin\theta-(1-a^2)J_0$	$2\pi\{1-(1-a^2)^{1/2}\}$
$a^2I^2\sin^2\theta=aJ_2\sin\theta$	$-\theta+J_0+J_1$	$2\pi\{1-(1-a^2)^{1/2}\}/(1-a^2)^{1/2}$
$a^2I\cos^2\theta$	$-\theta+a\sin\theta+J_0$	$2\pi\{1-(1-a^2)^{1/2}\}/(1-a^2)^{1/2}$
$a^2I^2\cos^2\theta$	$\{(1-a^2)\theta-(1-2a^2)J_0-J_1\}/(1-a^2)$	$2\pi\{(1-a^2)^{3/2}-(1-2a^2)\}/(1-a^2)^{3/2}$
$a^2I\sin\theta\cos\theta=aJ_1\cos\theta$	$-a\cos\theta-\log I$	0
$a^2I^2\sin\theta\cos\theta=aJ_2\cos\theta$	$\log I-I$	0

and OC the eccentricity e. The radius of the journal is r and that of the bearing $(r+\delta)$. The journal rotates around C, but at the same time C is in motion with respect to O. For our present purpose it is convenient to regard this motion as a combined rotation and growth of OC. The rotation of the shaft is ω, and that of the eccentricity ω_e.

The line of centres cuts the journal in A, B, and the bearing at A′, B′ ; AA′ is the maximum film thickness and BB′ the minimum. P is any point on the journal periphery, whose position is specified by the angle $AOP=\theta$. At this point the thickness of the film is

$$h \doteqdot (\delta + e\cos\theta) = \delta(1+a\cos\theta) = \delta/\mathrm{I}. \qquad (4.01)$$

The motion of the journal surface at the point P has components :

Tangentially forwards,

$$\mathrm{U} = \omega r - \omega_e \delta a \cos\theta + \delta \sin\theta \; da/dt, \quad . \quad . \quad (4.02)$$

and radially outwards,

$$\mathrm{V} = -\omega_e \delta a \sin\theta - \delta \cos\theta \; da/dt. \quad . \quad . \quad (4.03)$$

If Q be the volume flow of fluid, per unit axial length of journal, across the film at P, then

$$dQ/d\theta = \mathrm{V}r = -\omega_e r\delta a \sin\theta - r\delta \cos\theta \; da/dt, \quad (4.04)$$

$$\therefore \qquad \mathrm{Q} = \mathrm{Q}_0 + \omega_e r\delta a \cos\theta - r\delta \sin\theta \; da/dt. \quad . \quad (4.05)$$

Q_0 is a constant for all values of θ with fixed values of a, ω, and ω_e, but changes when any of these three quantities are varied.

The origin of coordinates is to be taken at P, the x-axis being drawn along the tangent in the direction of the motion $j\omega r$, and the y-axis radially outwards.

We shall make the customary assumptions, namely :—

(a) The axial length of the bearing is sufficient to permit us to neglect the endwise motion of the oil due to end leakage.

(b) The oil pressure is constant throughout the thickness of the film along a radius ; that is, $dp/dy=0$.

(c) The inertia of the oil itself may be left out of account.

(d) The viscosity of the oil is the same everywhere.

If p be the oil pressure at P, the theory of hydrodynamics then gives us *

$$dp/dx = \lambda \; d^2u/dy^2, \quad . \quad . \quad . \quad . \quad (4.06)$$

* See, for instance, Boswell [6] or Lamb [7].

where λ is the viscosity of the oil, and u its velocity in the x direction.

But $u=U$ when $y=0$, and $u=0$ when $y=h$. Hence,

$$u = (1/2\lambda)(dp/dx)\ y(y-h) + U(h-y)/h, \quad (4.07)$$

$$du/dy = (1/2\lambda)(dp/dx)\,(2y-h) - U/h \quad . \quad . \quad . \quad (4.08)$$

$$= -(1/2\lambda)(dp/dx)\,h - U/h \quad \text{when } y=0. \quad (4.09)$$

Also,

$$Q = \int_0^h u\,dy \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.10)$$

$$= \left[(1/2\lambda)(dp/dx)(\tfrac{1}{3}y^3 - \tfrac{1}{2}y^2 h) + U(hy - \tfrac{1}{2}y^2)/h\right]_0^h \quad (4.11)$$

$$= -(1/12\lambda)\,h^3\,(dp/dx) + \tfrac{1}{2}Uh. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.12)$$

Hence,

$$dp/dx = 6\lambda\{U/h^2 - 2Q/h^3\} = (6\lambda/\delta^3)\{U\delta I^2 - 2QI^3\}. \quad (4.13)$$

Thus,

$$(\delta^3/6\lambda r)(dp/d\theta)$$
$$= (\omega r\delta - \omega_e\delta^2 a\cos\theta + \delta^2\sin\theta\ da/dt)\ I^2$$
$$-2(Q_0 + \omega_e r\delta a\cos\theta - r\delta\sin\theta\ da/dt)\ I^3. \quad (4.14)$$

The only terms on integrating which do not vanish between the limits 0 and 2π are those involving J_0. Since p is the same for $\theta=2\pi$ as for $\theta=0$, the coefficient of J_0 must therefore be zero. Hence,

$$0 = \omega r\delta/(1-a^2) + \omega_e\delta^2 a^2/(1-a^2) - Q_0(2+a^2)/(1-a^2)^2$$
$$+ \omega_e r\delta \times 3a^2/(1-a^2)^2 \quad . \quad . \quad . \quad . \quad . \quad (4.15)$$

$$= (1-a^2)\omega r\delta + a^2(1-a^2)\omega_e\delta^2 - (2+a^2)\,Q_0 + 3a^2\omega_e r\delta.$$
$$. \quad . \quad . \quad (4.16)$$

Hence,

$$Q_0 = \delta\lceil r\{(1-a^2)\omega + 3a^2\omega_e\} + a^2(1-a^2)\omega_e\delta\rceil \div (2+a^2)$$
$$. \quad . \quad . \quad (4.17)$$

$$\doteqdot r\delta\{(1-a^2)\omega + 3a^2\omega_e\} \div (2+a^2). \quad . \quad . \quad . \quad . \quad (4.18)$$

Integrating, and remembering that the J_0 terms vanish, we get

$$\{(1-a^2)^2\delta^3/6\lambda r\}(p-p_0)$$
$$= -\omega r\delta(1-a^2)J_1 - \omega_e\delta^2(1-a^2)J_1 + \delta^2\{(1-a^2)^2/a\}I\ da/dt$$

$$+Q_0\{3J_1+(1-a^2)J_2\}-\omega_e r\delta\{(1+2a^2)J_1+(1-a^2)J_2\}$$
$$+r\delta\{(1-a^2)^2/a\}I^2\,da/dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.19)$$

$$=\{3Q_0-(1-a^2)\omega r\delta-(1+2a^2)\omega_e r\delta-(1-a^2)\omega_e\delta^2\}J_1$$
$$+(1-a^2)\{Q_0-\omega_e r\delta\}J_2+\{(1-a^2)^2/a\}\{\delta^2 I+r\delta I^2\}da/dt.$$
$$. \quad . \quad . \quad (4.20)$$

$$\therefore \quad (\delta^2/6\lambda r)(p-p_0)$$
$$=[\{r(\omega-2\omega_e)-2\delta\omega_e\}J_1+\{r(\omega-2\omega_e)+a^2\delta\omega_e\}J_2]$$
$$\div(2+a^2)+a^{-1}(\delta I+rI^2)\,da/dt \quad . \quad . \quad . \quad (4.21)$$

$$=\{r(\omega-2\omega_e)(J_1+J_2)-\delta\omega_e(2J_1-a^2J_2)\}\div(2+a^2)$$
$$+a^{-1}(\delta I+rI^2)\,da/dt. \quad . \quad . \quad (4.22)$$

The component normal to the eccentricity of the force due to the pressure, on a length L of the journal, is

$$F_{np}=\int_0^{2\pi} p\sin\theta\,.\,Lr\,d\theta = Lr\int_0^{2\pi}(p-p_0)\sin\theta\,d\theta \quad . \quad (4.23)$$

$$=[12\pi\lambda Lr^3a/(2+a^2)(1-a^2)^{\frac{1}{2}}\delta^2]$$
$$\times[(\omega-2\omega_e)+\omega_e(\delta/r)\{(2-a^2)$$
$$-(2+a^2)(1-a^2)^{\frac{1}{2}}\}/a]. \quad . \quad . \quad (4.24)$$

Since δ is only a small fraction of r, the last term may be neglected except when ω_e differs only a little from $\frac{1}{2}\omega$. When the oil drag is allowed for, as shown below, this term disappears but is replaced by another of the same order. Thus, except when ω_e is close to $\frac{1}{2}\omega$, we may write

$$F_{np}\doteqdot[12\pi\lambda Lr^3/\delta^2][\omega-2\omega_e][a/(2+a^2)(1-a^2)^{\frac{1}{2}}]. \quad (4.25)$$

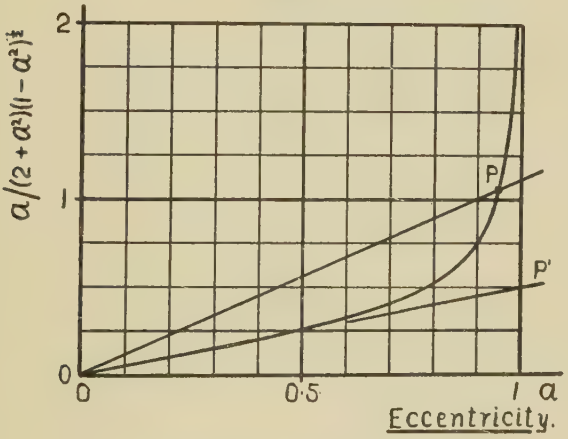
The expression within the first pair of square brackets is constant for a given bearing with a given lubricant; that enclosed by the second pair depends upon the rotations of the shaft and of the whirl; the third one takes account of the eccentricity.

The product $(2+a^2)(1-a^2)^{\frac{1}{2}}$ varies between 2 when there is no eccentricity and zero when $a=1$, but it does not begin to differ seriously from the former value until a exceeds 0·5, for which it has the value 1·949. Consequently, the normal oil force may be assumed proportional to the eccentricity so long as a is less than $\frac{1}{2}$, but beyond that the force increases more and more rapidly until it becomes infinite with $a=1$, when the journal is rubbing on the brass.

It is probable that our theory would not hold quite up to the rubbing condition, but in any case we shall suppose that the normal force vanishes at some whirl speed not far from half the shaft speed.

The function which takes account of the eccentricity in equation (4.25) has been plotted in fig. 2. The ordinates represent the force acting on the journal normal to the eccentricity to a scale which is proportional to $(\omega - 2\omega_s)$.

Fig. 2.



Variation of oil force with eccentricity.

The component of the oil-pressure force along the eccentricity is

$$F_{ep} = \int_0^{2\pi} p \cos\theta \,.\, Lr\, d\theta = Lr \int_0^{2\pi} (p - p_0) \cos\theta \, d\theta \quad (4.26)$$

$$= -(12\pi\lambda Lr^2/\delta^2) \lfloor \delta\{1-(1-a^2)^{\frac{1}{2}}\}/a^2(1-a^2)^{\frac{1}{2}} + r/(1-a^2)^{\frac{3}{2}} \rfloor \, da/dt. \quad (4.27)$$

$$\doteqdot -[12\pi\lambda Lr^3/\delta^2](1-a^2)^{-\frac{3}{2}} \, da/dt. \quad . \quad . \quad . \quad . \quad (4.28)$$

Thus the oil force along the eccentricity is zero when there is no radial movement of the journal centre. Consequently, the oil film cannot sustain indefinitely any force along the line of centres.

The small term which has been neglected is doubled when the oil drag is allowed for.

5. *Force on Journal due to Oil Drag.*

In addition to the force arising from the oil pressure, there is another caused by the frictional drag of the fluid on the journal. Except when ω_e is in the neighbourhood of $\frac{1}{2}\omega$, this second force is small compared with the first; in estimating it we may therefore safely neglect the terms involving δ^2 in comparison with those involving $r\delta$.

The tangential stress on the journal surface is then

$$q = \lambda(du/dy)_{r=0} = -\tfrac{1}{2}(dp/dx)h - \lambda U/h \quad . \quad . \quad . \quad (5.01)$$

$$= -3\lambda(U/h - 2Q/h^2) - \lambda U/h \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.02)$$

$$= \lambda(6Q/h^2 - 4U/h) = (6\lambda/\delta^2)(QI^2 - \tfrac{2}{3}U\delta I) \quad . \quad (5.03)$$

$$= (6\lambda r/\delta)[\{(1-a^2)\omega + 3a^2\omega_e\}I^2/(2+a^2) + \omega_e a I^2 \cos\theta - I^2 \sin\theta\,(da/dt) - \tfrac{2}{3}\omega I] \quad . \quad (5.04)$$

$$= \{6\lambda r/\delta(2+a^2)\}[\omega\{(1-a^2)I^2 - \tfrac{2}{3}(2+a^2)I\} + \omega_e\{3a^2I^2 + (2+a^2)aI^2\cos\theta\} - (2+a^2)I^2 \sin\theta\,(da/dt)]. \quad . \quad . \quad . \quad . \quad . \quad (5.05)$$

The component normal to the eccentricity of the force due to the friction, on a length L of the journal, is

$$F_{nf} = \int_0^{2\pi} q\cos\theta \,.\, Lr\,d\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.06)$$

$$= \{12\pi\lambda Lr^2/\delta\, a(2+a^2)(1-a^2)^{\frac{1}{2}}\} \times [\omega\{-a^2 + \tfrac{2}{3}(2+a^2)[1-(1-a^2)^{\frac{1}{2}}]\} - \omega_e\{3a^4 + (2+a^2)[(1-2a^2) - (1-a^2)^{3/2}]/(1-a^2)\}] \quad . \quad . \quad . \quad (5.07)$$

$$= \{12\pi\lambda Lr^2/\delta a(2+a^2)(1-a^2)^{\frac{1}{2}}\} \times [\omega\{4 - a^2 - 2(2+a^2)(1-a^2)^{\frac{1}{2}}\}/3 - \omega_e\{(2-a^2) - (2+a^2)(1-a)^{\frac{1}{2}}\}] \quad . \quad . \quad . \quad (5.08)$$

The ω_e term is exactly equal and opposite to the corresponding small term in the expression for the oil-pressure force, and the other term is of the order δ/r compared with that force.

The component along the eccentricity is

$$F_{ef} = \int_0^{2\pi} q\sin\theta\, Lr\,d\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.09)$$

$$= -[12\pi\lambda Lr^2/\delta][\{1-(1-a^2)^{\frac{1}{2}}\}/a^2(1-a^2)^{\frac{1}{2}}]\, da/dt. \quad . \quad . \quad (5.10)$$

This is equal to the small term in the expression for the radial force due to the oil pressure.

6. *Whirl of Journal with Rigid Rotor and no Transverse Load.*

There is no difficulty in writing down the differential equations for the motion of the centre of the journal on any given assumptions as to the inertia and other forces associated with that motion, but their nature is such that an exact solution, or even a reasonably approximate one, seems unattainable. But a good qualitative idea of what happens can be given without such solution.

Suppose, to begin with, that the rotor is rigid and that it partakes of the same motion as the journal. The velocity and acceleration upon which the frictional and inertia forces depend will then be the same as those of the journal centre.

Now, let the shaft be vertical and free from transverse load. For steady equilibrium, the journal must be concentric with the bearing, for in that position $a=0$ and the force exerted by the oil is zero.

Any accidental displacement of the rotor from this position will bring about an oil force pushing the journal forwards, with the result that the rotor axis begins to revolve round O. This acceleration will continue until $(\omega-2\omega_e)$ becomes small enough to reduce the oil force to that required to balance the external friction.

Meanwhile, the centrifugal force has been sending the journal out from the centre, which increases a and with it the forward driving force. There is a frictional force opposing this outward movement, but as it vanishes along with that movement, the oil film cannot support the centrifugal force of the whirl, and the journal will ultimately push its way through the film and rub on the brass.

Thus with a rigid rotor without transverse load, the journal will whirl with a radius equal to the radial clearance between it and the brass, and a whirl rotation approximately equal to half that of the shaft.

Since there is actual contact between the journal and the bearing, this phenomenon explains some of the troubles experienced with sleeve bearings.

7. *Whirl of a Horizontal Journal with a Rigid Rotor.*

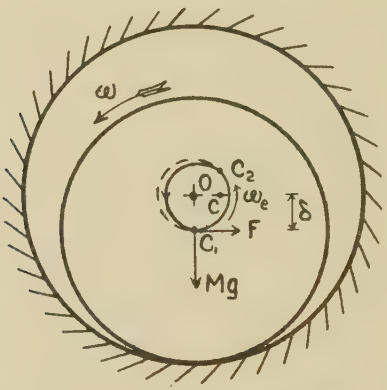
When the shaft is horizontal, as in fig. 3, the weight of the rotor puts a transverse load on the bearing and forces the journal into contact with the brass when there is no

rotation. The journal centre is now at C_1 vertically below O by the distance δ. The circle through C_1 with O as centre marks the boundary of the region within which the journal centre can move.

At a given speed, the point of static equilibrium for the journal centre is C, where OC is horizontal and of the length given by equation 4.25. But the equilibrium is again unstable.

Consider what happens to the journal centre whilst the rotor is being run up to speed. As soon as the oil film is formed between the journal and the brass, a horizontal force is exerted by the oil, which is very large because $a \doteqdot 1$. The journal is thus driven forwards, and at first

Fig. 3.



Journal of horizontal rigid rotor.

it remains in contact with the bearing because of the centrifugal force and the radial component of the weight.

But at some point C_2 above the horizontal diameter of the bearing, the centrifugal force is just balanced by the radial (with respect to OC_2) component of the weight. During its further forward movement the journal falls away from the brass, and its centre traces out a path something like that shown by the full line.

The journal will strike the bearing somewhere on its lower half and the same process will be repeated indefinitely, possibly accompanied by a certain amount of vibration at each blow.

C_2 lies on the horizontal diameter of the bearing when the whirl rotation is very small, and travels round the

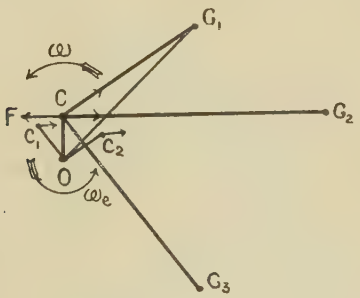
circle as the whirl goes faster. It is vertically over O when $\omega_e^2 = g/\delta$, and at greater whirl speeds than this the centrifugal force is sufficient to hold the journal against the bearing, and the action then becomes identical with that when there was no transverse load.

8. *Whirl of Journal of Elastic Rotor without Transverse Load.*

When the mass is connected to the journal through an elastic shaft, the motion of the c. g. is no longer the same as that of the journal centre, and the centrifugal force does not act along OC.

The oil-induced whirl of the journal induces, in turn, a whirl of the rotor with the same frequency. Because of

Fig. 4.



Elastic forces on journal.

the friction opposing the rotor whirl, the c. g. lags behind the plane whose trace is OC by an amount which increases as the rotation of the whirl goes up.

The conditions are shown in fig. 4, where G is the projection, on the plane of the paper, of the c. g., which is, of course, at some distance along the rotor from the journal.

The shaft is deflected through the distance OG by the rotor whirl, but as the journal is at the same time deflected by the amount OC, the net deflexion of the shaft is CG. The force due to the inertia and friction of the rotor is transmitted to the journal by the elasticity of the shaft and consequently lies along CG.

At low whirling speeds, as at G_1, the deflexion lags less than 90°. Consequently, the elastic force has a component along OC which increases the eccentricity and thereby augments the driving force and through it the rotation

of the journal whirl. The rotation of the rotor whirl must follow suit if the conditions be maintained.

At a certain speed, practically coincident with the critical speed of the rotor, CG is at right angles to OC, as at G_2 ; the elastic force is then in line with the oil force, and if they be also equal to one another there will be the equilibrium.

At higher whirling speeds, as at G_3, the elastic force has a component along CO which reduces the eccentricity and thereby diminishes the driving force and slows the whirl.

In the position G_2, if the oil force should exceed the elastic force, the journal whirl is accelerated ; but immediately the journal centre get ahead, as at C_1, the elastic force begins to pull it towards the centre of the bearing, and in this way the eccentricity is reduced until there is equilibrium.

If the elastic force be the greater, the converse actions take place, for with the journal centre behind, as at C_2, the elastic force has an outward component.

Thus, the oil-induced whirl in an elastic rotor runs at about half shaft speed until the whirl reaches the critical speed ; but any further increase of shaft speed does not affect the speed of the whirl.

With steady conditions the radius of the rotor whirl and the consequent elastic force are proportional to the eccentricity OC which is its cause. This elastic force is shown by the straight line OP in fig. 2. The point P where it cuts the curve gives the point of equilibrium.

The relative force scales of the straight line and curve vary with $(\omega - 2\omega_e)$. If we make the same curve do for all speeds by a suitable change of force scale, OP would be vertical with $\omega = 2\omega_e = 2\omega_0$, and it would slope less and less as the speed goes up. When OP is vertical, it cuts the curve at infinity, where $a = 1$; as its slope is diminished, P falls at a smaller and smaller value of a.

Thus, the eccentricity of the journal, and also the radius ρ of the corresponding rotor whirl, get smaller and smaller as the shaft speed is raised above twice its critical value. At a certain limiting speed, OP lies along the initial tangent to the curve ; P then goes to O and the whirl disappears.

If 2α be the frictional constant for the rotor whirl (friction supposed proportional to velocity) and ρ is the radius of that whirl at the critical speed ω_0, then

$$\rho \doteq (\omega_0/2\alpha)e = (\omega_0/2\alpha)\delta a. \quad . \quad . \quad . \quad (8.01)$$

The corresponding elastic force acting on the journal is

$$F_e = M\omega_0^2\rho = M(\omega_0^3/2\alpha)\delta a. \quad . \quad . \quad . \quad (8.02)$$

For equilibrium, this force must be balanced by the oil force, and on the initial tangent $(2 + a^2)(1 - a^2)^{\frac{1}{2}} = 2$. Hence, the limiting shaft speed, above which there is no oil-induced whirl, is given by the equation

$$(6\pi\lambda L r^3/\delta^2)(\omega - 2\omega_0) = M(\omega_0^3/2\alpha)\delta \quad . \quad . \quad (8.03)$$

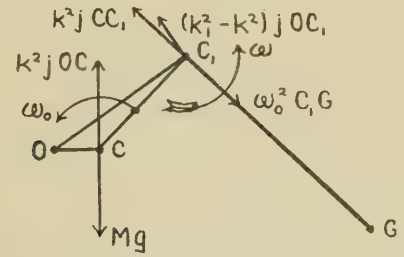
Or,
$$\omega = 2\omega_0 + M\omega_0^3\delta^3/12\pi\alpha\lambda L r^3. \quad . \quad . \quad . \quad (8.04)$$

Notice particularly how rapidly this limiting speed goes up as the bearing clearance is increased.

9. *Whirl of Horizontal Journal with Elastic Rotor.*

In the case of the loaded journal, as with the unloaded one, the elasticity of the shaft makes very little difference so long as the whirling speed is less than the critical speed of the

Fig. 5.



Whirl of horizontal journal with elastic rotor.

rotor. The journal whirls to the extent permitted by the clearance, but the response of the rotor is comparatively small until we approach resonance between the whirling speed and the critical speed.

We shall therefore confine our attention to the shaft running above twice its critical speed, in which case any whirl due to the oil rotates very nearly at the critical speed.

In fig. 5, C is the point of static equilibrium for the journal centre and C_1 its actual position. If C be close to O, compared with the distances OC_1 and CC_1 (remember, however, that OC_1 cannot exceed δ), we shall not be very far wrong if we assume that these two lengths are the same. Thus, with a small transverse load, the conditions are similar to those with no transverse load except that the centre of the whirl is displaced from O to C, and the space available for journal whirling on that side is correspondingly reduced.

With static equilibrium the oil force balances the weight and its amount is $\kappa^2 j.\,OC$, where j denotes "90° ahead of." At C_1 it is $\kappa_1{}^2 j.\,OC_1$. If κ and κ_1 were alike, the force to be balanced by the elastic reaction of the shaft would be $\kappa^2 j.\,CC_1$.

But κ and κ_1 are not alike because of the changes in the factor $(\omega - 2\omega_e)/(2+a^2)(1-a^2)^{\frac{1}{2}}$. As we have already seen, the divisor varies little until $a=\frac{1}{2}$, but after that it diminishes more and more rapidly and becomes zero when $a=1$.

With equilibrium at C, ω_e is zero, whereas at C_1 it has an average value of somewhere about ω_0 but fluctuates, sometimes to a large extent, during each revolution of OC_1. Thus, when OC_1 is greater than OC, the multiplier and divisor are both smaller for κ_1 than for κ, and it is impossible to make any general statement as to which is the greater.

Suppose, as a first approximation, that the journal is whirling round C with the rotation ω_0 at such a radius CC_1 that the oil force $\kappa^2 j.\,CC_1$ is balanced by the rotor whirl forces after the rotor whirl has attained a steady state. There is a discrepancy force $(\kappa_1{}^2 - \kappa^2) j.\,OC_1$ which produces a subsidiary disturbance. This discrepancy force rotates along with OC_1 and it also oscillates in magnitude.

As a second approximation, we may assume that the discrepancy force has a constant rotation ω_0, so that its magnitude consists of a constant term plus a harmonic one whose phase velocity is also ω_0.

The constant term must be balanced by the elastic force of a small additional rotor whirl of the same rotation as the first, with which it must be combined vectorially. The harmonic term gives rise to two rotor whirls of rotations $2\omega_0$ and zero, but their amplitude will be small because they are far from resonance.

Thus, the discrepancy forces will be spent mainly in accelerating the journal by deflecting the shaft and will produce only minor effects on the body of the rotor.

As the journal, in the course of its whirl, approaches the near side of the bearing, the oil force increases and sends the journal ahead. The elastic force then pulls the journal in and thus prevents actual contact, although the mean radius of the whirl may be greater than the distance from the centre of the whirl to the boundary circle.

Thus the rotor whirl will not differ very greatly from that without transverse load, although the journal whirl is considerably different. With large transverse loads C would be some distance out and leave little room for whirling on that side. We may therefore expect the mean radius of the

journal whirl to be reduced by large transverse loads and the rotor whirl to be diminished accordingly.

As the shaft speed is raised, C moves towards the centre of the bearing and the conditions approximate more closely to those with no transverse load.

10. *Comparison with Newkirk and Taylor's Experimental Results.*

Newkirk and Taylor [4] tested one of their models in the vertical position with the upper end supported by a ball bearing and a single journal bearing at the bottom. Their graph for this test (their fig. 7) shows a peak of 7 mils double amplitude at 800 r. p. m.; one of 40 mils at 1520 r. p. m., and a sharp rise to 50 mils at 2500 r. p. m., followed by a gradual increase as the speed was raised further. The diametral clearance of the bearing was 8 mils.

The first resonance occurs at the critical speed, and is due to unbalance. The second is the "oil resonance whirl" we have been considering. Between these speeds the whirl is small and runs at approximately half the shaft speed, whereas it ran at the critical speed, or very nearly so, at all shaft speeds above the oil resonance.

All of these agree with our theory, except that we should have expected the amplitude at oil resonance to be greater, say about 100 times the clearance. But the third rise and the subsequent vibration at all higher speeds within the limits of their test cannot be explained on our theory at all. This high speed whirling, which also runs at, or near, the critical speed, they term "whipping." It is probable that it always did run at the critical speed corresponding to the actual amplitude, which speed was somewhat higher than at lower amplitudes because of the restraint offered by the bearing to the tilting of the journal.

We must therefore suppose that our theory breaks down when the shaft speed is pushed beyond some limit at which whipping begins, and the most probable explanation is that at this point the oil ceases to flow in streamlines and breaks up into eddies.

Since the whirl rotates at the critical speed, equilibrium requires the oil force to be perpendicular to the eccentricity. Moreover, as the rotor whirl now increases with the shaft speed, the curve corresponding to fig. 2 must be convex upwards instead of downwards. The author is unable to say whether the oil force produced by a turbulent flow between the journal and the bearings would agree with these requirements or not.

The same rotor, but with the journals reduced from 1½ inch to 1 inch diameter, was also run horizontally in two journal bearings. The oil resonance then failed to appear, possibly because the two journals whirled in opposite phases. Whipping began at lower speeds than before, at 1200 r.p.m. with 15 mils diametral clearance, at 1550 r.p.m. with 8 and 4 mils, and at 1700 r.p.m. with 2 mils.

As would be expected, the whirl amplitude was greater with the larger clearance, but all four curves seem to approach a common amplitude of 220 mils at 3600 r.p.m. This earlier start of whipping with larger clearances is what we should expect if turbulence be the cause.

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XIII. *Gravitation and Electricity.*—Part III.

By H. F. Willis, *B.Sc.**

§ 1.

THE present paper is concerned with the investigation of certain practical aspects of a theory of gravitation which has recently been published by Prof. G. H. Livens and Dr. Irene E. Viney. For the sake of completeness a brief account of the formulation of this theory is here given.

Gravitational fields are attributed to some substance contained in the structure of matter. This substance is supposed

* Communicated by Prof. G. H. Livens.

to be akin to electricity, and it is termed "gravity." The volume density of a charge of gravity is denoted by τ. At each point of space is defined a four-vector, τ_r, whose components are τv_1, τv_2, τv_3, $i\tau$, where v_1, v_2, v_3 are the components of velocity of gravity at the point concerned.

The state of the gravitational field at any point is defined by a symmetric tensor G_{rs}, which is itself derived from four potential functions, $\psi_1, \psi_2, \psi_3, \psi_1$, according to the equations

$$G_{rs} = -\left(\frac{\partial \psi_r}{\partial x_s} + \frac{\partial \psi_s}{\partial x_r}\right),$$

where the coordinates used are x_1, x_2, x_3, x_4, connected with real space and time coordinates by

$$x_1 = x, \qquad x_2 = y, \qquad x_3 = z, \qquad x_4 = ict.$$

The tensor G_{rs} is related to the distribution of gravity by the four field equations

$$\frac{\partial G_{rs}}{\partial x_s} = -\tau_r, \qquad r = 1, 2, 3, 4.$$

If the potentials ψ are assumed to satisfy the auxiliary relation

$$\frac{\partial \psi_r}{\partial x_r} = 0,$$

then the above field equations may be reduced to the form

$$\Box^2 \psi_r = \tau_r, \qquad r = 1, 2, 3, 4,$$

where

$$\Box^2 \equiv \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} + \frac{\partial^2}{\partial x_4^2}.$$

The dynamics of a system may be summed up in the form of a variational principle by taking as the Lagrangian Function the volume integral of $-\frac{1}{4} G_{\alpha\beta} . G_{\alpha\beta}$ over the whole of the field. Corresponding to this the forcive per unit volume of gravity in the field has components

$$F_r = F_{rs} \tau_s, \qquad r = 1, 2, 3,$$

where

$$F_{rs} = -\left(\frac{\partial \psi_r}{\partial x_s} - \frac{\partial \psi_s}{\partial x_r}\right).$$

The fourth component, F_4, represents the rate of working:

$$F_1 v_1 + F_2 v_2 + F_3 v_3.$$

The forcive is also expressed in the Stress-Momentum form, and it is found that the stress-energy tensor is

$$S_{rs} = G_{\alpha s} \frac{\psi_\alpha}{\partial x_r} + \psi_r \tau_s + \tfrac{1}{4} \delta_{rs} (G_{\alpha\beta} G_{\alpha\beta})$$

from which are derived:—

(i.) The energy density as $-S_{44}$.

(ii.) The momentum components $\frac{1}{c}(S_{14}, S_{24}, S_{34})$.

(iii.) The energy flux components $\frac{c}{i}(S_{41}, S_{42}, S_{43})$.

§ 2.

In the following we shall evaluate certain of the physical quantities formulated above for certain special cases. By so doing we shall be able to bring to light some of the properties of the substance "gravity" which are implied by the given field equations. The problems dealt with, and the methods employed in their solution will all be familiar in electrical theory.

It is clear that all our evaluations will require a knowledge of the values of the potentials at all points of space appropriate to the distributions of gravity involved. All such distributions will usually be in motion, and consequently it is the retarded potentials which we shall have to determine, and we shall now discuss how this can be done. The determinations can be made accurately when the motions involved are uniform, and the values thus obtained will be very nearly true for the quasi-stationary or slowly varying type.

Consider in the first case the field due to a perfectly general distribution of density τ (not necessarily constant) which, however, is moving with the same velocity at all points of space. This velocity we shall take to be along the X axis and of magnitude v.

The potentials ψ under all circumstances satisfy the equations

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\psi_r=\tau_r.$$

These equations may now be solved by the same device used in the electrical case. The field may naturally be looked upon as the uniform translation, with velocity v, of a static field. It follows that the change in ψ at a fixed point during a time interval dt is exactly the same as the change in ψ at a fixed instant over a space interval $dx=-v.dt$ from the point concerned. In other words, the differential

$\frac{\partial}{\partial t}$ in our field may be replaced by $-v\frac{\partial}{\partial x}$. Making this substitution, our field equations become

$$\left(\alpha^2\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi_r=\tau_r,$$

where $$\alpha^2=1-v^2/c^2.$$

Changing now the coordinates to the set

$$x'=x/\alpha, \qquad y'=y, \qquad z'=z,$$

the equations become

$$\left(\frac{\partial^2}{\partial x'^2}+\frac{\partial^2}{\partial y'^2}+\frac{\partial^2}{\partial z'^2}\right)\psi_r=\tau_r=\frac{1}{\alpha}\tau_r',$$

where $\tau_r'=\alpha\tau_r$ corresponds to the modified density in the new coordinates. The equation we have now derived is simply the Laplacian equation in the new coordinates, and its general solution is accordingly

$$\psi_r=-\frac{1}{4\pi\alpha}\int\frac{\tau_r'\,dv'}{r'},$$

where $r'^2=x'^2+y'^2+z'^2$ and $dv'=dx'.dy'.dz'$.

Transforming the integral back to the original coordinates, we get

$$\psi_r=-\frac{1}{4\pi\alpha}\iiint\frac{\tau_r\,dx\,dy\,dz}{\sqrt{x^2/\alpha^2+y^2+z^2}}.$$

Thus we have secured the solution for a distribution moving with one velocity v. If we have the more general case where systems τ_1, τ_2, τ_3, ... are moving with respective uniform velocities v_1, v_2, v_3, ... then the ψ for any point may be obtained by evaluating it for each of the separate systems in turn, in the above manner, and then by summing all the results.

In the next paragraph we shall have to employ the values of the retarded potentials due to a sphere in uniform motion. These may readily be deduced from the previous general formula. Consider a sphere of gravity whose total amount is M. Following the analogy of the Lorentz electron, we shall assume that when in uniform motion this sphere undergoes a longitudinal contraction in the direction of motion of amount $(1-v^2/c^2)^{\frac{1}{2}}:1$. This assumption will also greatly simplify the solution of the problem, for it follows that in

the contracted space the distorted sphere, whose equation is actually

$$x^2(1-v^2/c^2)^{-1}+y^2+z^2=a^2,$$

becomes now $x'^2+y'^2+z'^2=a^2$,

and is thus a sphere of radius a. Thus our solution becomes

$$\psi_r=-\frac{1}{4\pi\alpha}\int\frac{\tau_r'\,dv'}{r'}=-\frac{1}{4\pi\alpha}\frac{\mathrm{M}_r}{r'}$$

for external points, M_r being the four-vector corresponding to the quantity M. Written in full, this solution is

$$\psi_1=-\frac{1}{4\pi\alpha c}\frac{\mathrm{M}v}{\sqrt{(x^2/\alpha^2+y^2+z^2)}},\qquad \psi_2,\ \psi_3=0,$$

$$\psi_4=-\frac{1}{4\pi\alpha}\cdot\frac{\mathrm{M}}{\sqrt{(x^2/\alpha^2+y^2+z^2)}}.$$

In the same way the potentials at internal points of the sphere may be readily secured. They are

$$\psi_r=-\frac{\mathrm{M}_r}{8\pi\alpha a}\left\{3-\frac{x^2/\alpha^2+y^2+z^2}{a^2}\right\}.$$

For the case of the spherical shell distribution we get precisely the same values for the potentials at external points, but at internal points they have the constant values

$$\psi_r=-\mathrm{M}_r/4\pi\alpha a.$$

§ 3.

We shall now calculate for a uniformly moving shell and solid sphere the various physical quantities associated with them. In each case the velocity will be taken to be along the X axis, and the Lorentz contraction will be assumed, so that our potential formulæ will be applicable.

The Lagrangian Function.

This, as we have seen, is the volume integral of $-\frac{1}{4}\mathrm{G}_{\alpha\beta}\mathrm{G}_{\alpha\beta}$. Expanding this, and remembering that $\psi_2=\psi_3=0$, it becomes

$$\begin{aligned}-\tfrac{1}{4}\{&\mathrm{G}_{11}^2+\mathrm{G}_{44}^2+2\mathrm{G}_{12}^2+2\mathrm{G}_{13}^2-2\mathrm{G}_{14}^2+2\mathrm{G}_{24}^2+2\mathrm{G}_{34}^2\}\\ &=-\left\{\left(\frac{\partial\psi_1}{\partial x_1}\right)^2+\left(\frac{\partial\psi_4}{\partial x_4}\right)^2+\frac{1}{2}\left(\frac{\partial\psi_1}{\partial x_2}\right)^2+\frac{1}{2}\left(\frac{\partial\psi_1}{\partial x_3}\right)^2\right.\\ &\quad+\frac{1}{2}\left(\frac{\partial\psi_1}{\partial x_4}\right)^2+\frac{1}{2}\left(\frac{\partial\psi_4}{\partial x_4}\right)^2+\frac{1}{2}\left(\frac{\partial\psi_4}{\partial x_2}\right)^2+\frac{1}{2}\left(\frac{\partial\psi_4}{\partial x_3}\right)^2\\ &\qquad\left.+\frac{\partial\psi_1}{\partial x_4}\cdot\frac{\partial\psi_4}{\partial x_1}\right\}.\end{aligned}$$

Taking now the case of a shell, it is clear that the constant potentials in its interior will yield no contribution to the final result. Substituting then the appropriate forms for the potentials at external points, we get ultimately

$$-\tfrac{1}{4}G_{\alpha\beta}G_{\alpha\beta}=M^2/32\pi^2r'^4.$$

This has to be integrated over the whole of space exterior to the shell. This gives us as the value of the Lagrangian Function

$$L=\frac{M^2}{32\pi^2}\iiint\frac{dx\,dy\,dz}{r'^4}.$$

Expressing this integral in terms of the previous set of coordinates $x'y'z'$, it becomes

$$L=\frac{M^2}{32\pi^2}\int_a^\infty\int_a^\infty\int_a^\infty\frac{a\,dx'\,dy'\,dz'}{r'^4}.$$

On further transforming to polar coordinates in this contracted space, defined by

$$x'=r'\sin\theta\cos\phi,\qquad y'=r'\sin\theta\sin\phi,\qquad z'=r'\cos\theta,$$

we get

$$L=\frac{aM^2}{32\pi^2}\int_a^\infty\int_0^\pi\int_0^{2\pi}\frac{\sin\theta}{r'^2}dr'\,d\theta\,d\phi,$$

which works out to

$$L=M^2a/8\pi a=M^2/8\pi\,.\,\sqrt{(1-v^2/c^2}.$$

If we consider now the case of the solid sphere, we see that there is an internal field, and that there will consequently be a contribution to the Lagrangian Function from this source. At external points, however, the field is exactly the same as in the previous case, so that the external contribution is unaltered. To get the internal contribution we simply have to take the forms for the potentials for internal points and repeat the above calculations. This contribution is found to be

$$M^2/40\pi a\,.\,\sqrt{(1-v^2/c^2)},$$

thus giving a total for the solid sphere of amount

$$L=3M^2/20\pi a\,.\,\sqrt{(1-v^2/c^2)}.$$

We may mention that the corresponding values for similar distributions of electricity of total amount e are

$$-e^2/8\pi a\sqrt{(1-v^2/c^2)}$$

for the shell distribution and

$$-3e^2/20\pi a\sqrt{(1-v^2/c^2)}$$

for the solid spherical distribution.

The Energy.

The energy density is

$$W=-S_{44}=-\left\{G_{\alpha 4}\frac{\partial\psi_\alpha}{\partial x_4}+\psi_4\tau_4+\frac{1}{4}G_{\alpha\beta}G_{\alpha\beta}\right\}.$$

We have already evaluated the term $-\frac{1}{4}G_{\alpha\beta}G_{\alpha\beta}$. Also the term $\psi_4\tau_4$ will be zero everywhere outside the sphere. Consider then the term

$$-G_{\alpha 4}\frac{\partial\psi_\alpha}{\partial x_4}=\left(\frac{\partial\psi_\alpha}{\partial x_4}+\frac{\partial\psi_4}{\partial x_\alpha}\right)\frac{\partial\psi_\alpha}{\partial x_4},$$

which in our simple case becomes

$$\left(\frac{\partial\psi_1}{\partial x_4}\right)^2+2\left(\frac{\partial\psi_4}{\partial x_4}\right)^2+\frac{\partial\psi_4}{\partial x_1}\cdot\frac{\partial\psi_1}{\partial x_4}.$$

Substituting for the ψ's this becomes

$$M^2v^2x^2/16\pi^2c^2\alpha^4a'^6.$$

If we integrate this over the exterior part of the shell, transforming the integral in the same way as before, we get

$$M^2v^2/12\pi a\alpha c^2.$$

We have now the third term to consider, namely, $-\psi_4\tau_4$. This is non-zero only on the surface of the shell, where, in contracted coordinates, its value is $-M\sigma'/4\pi a\alpha$, σ' being the surface density of the transformed surface, which is, of course, now a sphere. Integration over this sphere gives $-M\sigma' a/\alpha$. But σ' is clearly given by $4\pi a^2\sigma'=M$, so that our term becomes $-M^2/4\pi a\alpha$.

The total energy of the shell is accordingly the sum

$$E=\frac{M^2\alpha}{8\pi a}-\frac{M^2}{4\pi a\alpha}+\frac{M^2v^2}{12\pi a\alpha c^2}$$

$$=-\frac{M^2}{8\pi a}\frac{1+\frac{1}{3}\frac{v^2}{c^2}}{\sqrt{\left(1-\frac{v^2}{c^2}\right)}}.$$

In finding the energy of the solid sphere we have again

to consider the additional part contributed by the internal field, which works out to be

$$-\frac{M^2}{40\pi a}\cdot\frac{1+v^2/3c^2}{\sqrt{(1-v^2/c^2)}},$$

thus giving as the total energy

$$E=-\frac{3M^2}{20\pi a}\frac{1+v^2/3c^2}{\sqrt{(1-v^2/c^2)}}.$$

Here again our formulæ resemble the corresponding electrical formulæ, which are

$$+\frac{e^2}{8\pi a}\frac{1+v^2/3c^2}{\sqrt{(1-v^2/c^2)}} \quad \text{and} \quad +\frac{3e^2}{20\pi a}\frac{1+v^2/3c^2}{\sqrt{(1-v^2/c^2)}},$$

the only essential difference being one of sign.

The Momenta.

The components of momentum density are $\frac{1}{ic}(S_{14}, S_{24}, S_{34})$. It can easily be verified, and it is otherwise quite obvious, that the components S_{24} and S_{34} are zero. Our momentum is, therefore, $\frac{1}{ic}S_{14}$ along the axis Ox.

We have

$$\frac{1}{ic}S_{14}=\frac{1}{ic}\left\{G_{\alpha 4}\frac{\partial\psi_\alpha}{\partial x_1}+\psi_1\tau_4\right\}$$

$$=-\frac{1}{ic}\left\{\frac{\partial\psi_1}{\partial x_4}\frac{\partial\psi_1}{\partial x_1}+\frac{\partial\psi_4}{\partial x_1}\cdot\frac{\partial\psi_1}{\partial x_1}+2\frac{\partial\psi_4}{\partial x_4}\frac{\partial\psi_4}{\partial x_1}\right\}$$

$$+\frac{1}{ic}\psi_1\tau_4.$$

The first term is the only one non-zero in free space. Its value is

$$\frac{M^2v}{16\pi^2\alpha^4e^2}\frac{x^2}{(x^2/\alpha^2+y^2+z^2)^3}$$

for external points and

$$\frac{M^2v}{16\pi^2a\alpha^4c^2}\cdot x^2$$

for internal points in the case of the solid sphere.

When integrated up in the usual way the corresponding contributions are

$$M^2v/12\pi a\alpha c^2$$

from the external field and

$$M^2v/60\pi a\alpha c^2$$

from the internal field.

We must now consider the term $\frac{1}{ic}\psi_1\tau_4$, which in the case of the shell has to be integrated over its surface, and gives $-M^2v/4\pi a\alpha c^2$. For the solid sphere we have to integrate it throughout the volume of the sphere, and we get $-M^2v/20\pi a\alpha c^2$.

Combining these results, we have :—

$$\text{Momentum of shell} = \frac{M^2v}{12\pi a\alpha c^2} - \frac{M^2v}{4\pi a\alpha c^2}$$

$$= -\frac{M^2}{6\pi ac^2}\frac{v}{\sqrt{(1-v^2/c^2)}}.$$

$$\text{Momentum of solid sphere} = \frac{M^2v}{60\pi a\alpha c^2} - \frac{M^2v}{20\pi a\alpha c^2}$$

$$= -\frac{M^2}{5\pi ac^2}\frac{v}{\sqrt{(1-v^2/c^2)}},$$

which again differ only in sign from the corresponding electrical formulæ.

The Inertia.

From the fact that gravity possesses momentum it follows that it possesses the property of inertia. If a force F be applied to a spherical shell whose momentum we have already found to be $-M^2v/8\pi a\alpha$, then the resulting motion is given by the equation

$$\frac{d}{dt}\left\{-\frac{M^2v}{8\pi a\alpha}\right\} = F,$$

i. e.,

$$F = -\frac{M^2}{8\pi a\alpha^3}\cdot\frac{dv}{dt},$$

which shows that for a longitudinal force the shell has inertia

$$\mu_e = -\frac{M^2}{8\pi a\alpha^3}.$$

In the same way, as in the electrical case, we can show that the transverse inertia is

$$\mu_t = -\frac{M^2}{8\pi a\alpha}.$$

It should be pointed out that in deriving the inertia of the shell we have employed the momentum equation of motion. We might expect the same result to be deduced from the Lagrangian Function. This, however, is not found to be the case. The difference, as in the electrical case, can be attributed to the fact that the energy of the shell is in part due to forces of elastic nature which we have to suppose to exist in the structure of the shell in order to account for its stable configuration. Concerning this point reference may be made, for example, to Livens's 'Theory of Electricity' (p. 355).

§ 4.

We have now to examine the practical aspects of the calculations which we have made for the various physical quantities associated with a spherical distribution of gravity, and to examine in what way and to what extent the results may modify our existing concepts of these quantities.

We notice that all our formulæ are of the same type as the corresponding formulæ, except that they are invariably of the opposite sign. The reason for this continual difference in sign may be traced down to the fact that the stress-energy tensor of the gravity field, from which all our quantities are derived, has to be designed so as to account for an *attractive* force between particles of gravity. The corresponding electro-magnetic tensor, however, has to lead to a *repulsive* force between like charges of electricity.

We have found that for both the shell and solid sphere the energy, momentum, and inertia are all negative. It is further evident that these quantities will also be negative for distributions of gravity of any size and shape.

These results at first sight appear to be contrary to experience. Thus it is certain that a material body in any state of motion possesses positive kinetic energy, a positive amount of work having to be performed to establish its motion. But it must be emphasized that the substance denoted by "gravity" must be in no way confused with "matter." The two may possess entirely different properties. We have no direct experience of gravity, and so cannot assert what its properties actually are. In any case it is not difficult to account for the fact that the properties which our theory leads us to associate with gravity are not possessed by matter in bulk. We have only to remember that all matter contains as essential constituents charges of electricity which (as we shall see later) are enormously greater in magnitude than the charges of gravity with which they occur in a

single atom. But the physical quantities associated with the electric charges are positive, and may, therefore, be expected to counterbalance the negative properties of the gravity particles, and leave the complete structure with positive properties.

The negative inertia of gravity is a property which leads to some remarkable consequences, which are, however, probably worth a short discussion.

Remembering that the inertia of a particle is the factor which relates the magnitude of an applied force to the acceleration it produces in the particle, it follows that a negative inertia must be interpreted as implying that the acceleration is in the opposite sense to the applied force. In particular, if the particle is initially at rest, the subsequent motion is in the opposite direction to the force. If, therefore, we imagine two particles of gravity, initially at rest, each will exert a force of attraction upon the other, and will, consequently, begin to move apart from one another, just as though a repulsive force was in operation and the particles possessed positive inertias. This conclusion must not, of course, be confused with the observed behaviour of *material* particles which actually move towards one another. This is to be expected from the positive inertias of such particles.

Our previous conclusion may be generalized by saying that any distribution of gravity will tend to expand indefinitely under its own field in exactly the same way as we should expect a distribution of electricity to behave. In fact, from the similarity in behaviour of the two systems, it might be difficult in practice to determine which particular mechanism is actually in operation.

Another interesting circumstance arises if we consider the action between two particles possessing charges of gravity, but the one particle possessing positive and the other negative inertia. Such a system is realized in the case of a particle of gravity and a particle of neutral matter. Consider, then, two such particles initially at rest. Here again each exerts an attractive force upon the other, but the force on the material particle produces a motion in the same direction, whereas the force on the gravity particle produces a motion in the opposite direction. The result is that the two particles move in the same direction. It is interesting to note that if the numerical values of the two inertias are the same, the separation of the particles will not alter, and the motion will continue in this way with continually increasing velocity, with the particle of matter pursuing the

particle of gravity. At first sight it seems that there is created in this process an indefinite amount of kinetic energy, but we must remember that the motion of the one particle implies a negative energy which decreases with increasing velocity. This decrease is exactly counterbalanced by the increase in the energy of the material particle. Thus there is in effect a continual transfer of energy from the one particle to the other.

We shall not discuss any further the above considerations, but turn now to examine what consequences we may expect from the presence of gravity in the structure of the atom.

The ultimate units in the structure of matter, as we understand it at present, are the proton and the electron, which occur in pairs in the constitution of every neutral atom. The question immediately arises at this stage whether we are to expect particles of gravity to feature as additional units in the structure of matter, or whether all the charges of gravity involved are associated entirely with the proton or electron, or both.

The former possibility does not seem to be very likely for the following reasons. Particles of gravity, if they exist independent of protons and electrons, may either occur bound by forces to individual atoms or else completely free. In the latter case the application of a gravitational field to a material body would bring about a redistribution of the gravity particles, in much the same way as an electric field affects the free electrons of a conducting body. As a consequence of this we should not be able to calculate the attraction between large spheres of matter as if they operated at their centres, and such a circumstance, if it were true, would have been realized in the laboratory determinations of the gravitational constant. Thus we may conclude that particles of gravity do not occur free. On the other hand, it is difficult to imagine how they may be bound by field forces to individual atoms. We cannot suppose that they describe orbits round the central nucleus under the action of a charge of gravity associated with the nucleus, because such orbits would be hyperbolas. We are thus forced to conclude that gravity probably occurs only in the proton and electron.

It is important to know the relative magnitudes of the charges of gravity and electricity which occur in any atom. We shall consider the hydrogen atom, which is the simplest, being composed of one proton and one electron. Suppose that M is the total charge of gravity associated with the hydrogen atom, as measured in the Heaviside scheme of

units, which has been employed throughout the work. Then, from the formulation of the theory of gravitation, it is easily shown that the attractive force between two hydrogen atoms separated by a distance of 1 cm. is $M^2/4\pi$. This force can be otherwise expressed in terms of experimental constants. If N is Avagadro's number, then there are N atoms in each gram of hydrogen. The inertia of the hydrogen atom is accordingly 1/N gm. The force of attraction between two such atoms at unit distance apart is consequently γ/N^2, where γ is the gravitational constant. Hence we have

$$M^2/4\pi = \gamma/N^2,$$

$$\therefore \qquad M = \sqrt{(4\pi\gamma)}/N.$$

But we have the experimental values

$$N = 60 \times 10^{22}, \qquad \gamma = 6{\cdot}7 \times 10^{-8}.$$

Hence $$M = 7{\cdot}0 \times {}^{-27}.$$

As regards the charge E associated with either the proton or the electron, we have Millikan's value of $4{\cdot}774 \times 10^{-19}$ electrostatic units, so that in terms of Heaviside units

$$E = \sqrt{4\pi} \times 4{\cdot}774 \times 10^{-10} = 1{\cdot}7 \times 10^{-9}.$$

The quantity M determined above represents the sum of the charges of gravity associated with the proton and electron of the hydrogen atom. We have no knowledge, however, as to the way in which the total charge is divided between the two, and there appears to be no evidence to guide us in this direction. It is certain that experiments on the variation of the inertia of the electron with its velocity can tell us nothing, because of the similarity of the formulæ for the inertias of distributions of electricity and gravity. All that we can do at the present moment is to suppose that the charges of gravity belonging to the electron and proton are tM and $(1-t)$M respectively, where t is some number less than unity.

We have found that the gravity charge tM of the electron is very much less than the electric charge. This suggests that the presence of the gravity has an inappreciable influence on the inertia of the electron. Thus, if we imagine the gravity and electric charges of the electron to exist in the form of a single spherical shell distribution of radius a, then from our previous results the inertia of such a system is $(E^2 - t^2M^2)/6\pi a c^2$, provided that we assume that there is no action between the two fields present. This quantity differs from the electrical part alone by a ratio t^2M^3/E^2 whose value is less than 10^{-35}, as we see from the numerical values

for M and E. But it is not necessary to suppose that the radius of the gravity distribution is equal to that of the electrical part. If the former radius is reduced, the contribution of the gravity field becomes more significant ; in fact, by simply adjusting the two radii, we can make the inertia of the electron to be anything we like, positive or negative or even zero.

On the whole, then, we can say that our assumption of the existence of a new element in the constitution of matter involves probably no appreciable alteration in our views on atomic dynamics, which are bound to remain essentially electrical in character. Nevertheless, it is not impossible that sooner or later some modification of the purely electrical view may be required, and then it may be possible to test our present hypothesis. The recent discovery of the apparently non-electrical "neutron" may, for example, be a first step in this direction, as its high penetrating power suggests a much less intense field of action, which would, of course, be obviously the case if the action were gravitational.

XIV. *Bubble Formation in Glass Tubes.* *By* W. B. Mann, *B.Sc., A.R.C.S., and* R. W. B. Stephens, *B.Sc., A.R.C.S.**

[Plates VI. & VII.]

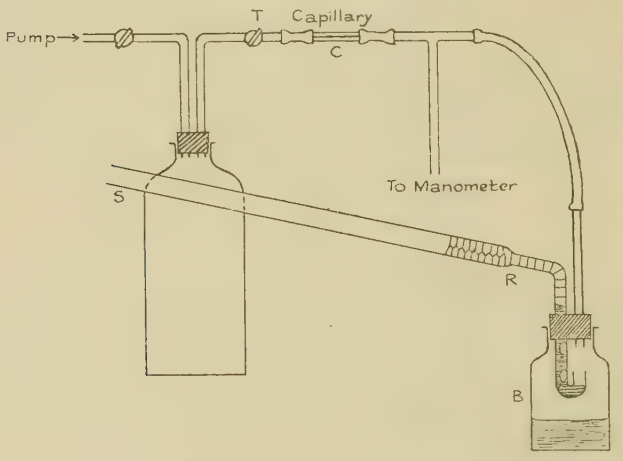
DURING the course of experiments in which a constant head of oil was employed it was observed that a series of oil-bubbles of remarkable regularity and stability was formed in one of the glass tubes of the apparatus. These bubbles, indeed, were of such interest that a simple arrangement was set up for the purpose of observing and photographing their formation.

The arrangement used to obtain the bubbles is shown in fig. 1. A large capacity glass bottle, in which air may be stored under pressure, is connected through a tap T and a short length of glass capillary tube C to a smaller bottle B. This bottle B is fitted with a rubber stopper, through which is inserted, in addition to the inlet tube, a glass U-tube terminating at its upper end in an inclined tube RS of about 2 cm. bore, and which is described hereafter as the bubble-tube. A suitable size of U-tube and bubble-tube for the illustration of the phenomena was found by experiment. The liquid in question was introduced into the U-tube by

* Communicated by Prof. H. S. Gregory, Ph.D., A.R.C.S., D.I.C.

pouring it down the bubble-tube, so that, on the depression of the liquid column in the shorter limb of the U-tube, the liquid level reached a convenient height in the other limb. Air was then allowed to bubble through the liquid at a suitable rate, this rate being controlled by appropriate choice of the capillary C and adjustment of the tap T. The excess pressure in B was indicated by a mercury manometer, and was varied during the course of the experiments between the limits of 1 and 3 cm. of mercury. The rate of formation of the bubbles was usually from fifty to eighty per minute.

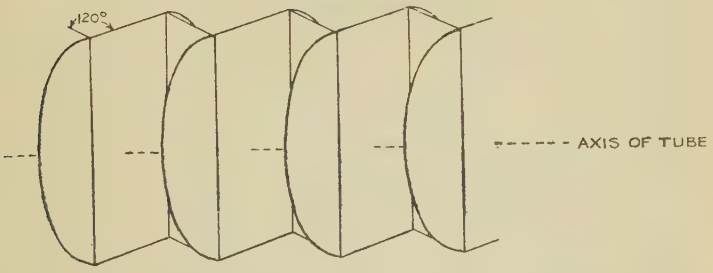
Fig. 1.



If the liquid level was below the juncture R of the U-tube and bubble-tube, then, as each bubble left the upper surface of the liquid, there was formed in general a circular film, the plane of which was perpendicular to the axis of the tube. This film moved along the tube, preserving its individuality until the junction R was reached, where, however, except in certain cases to be mentioned later, it coalesced with those films proceeding before and following after it. In this manner one continuous bubble system was formed, which moved slowly along the bubble-tube. This system consisted of a series of apparently plane films lying along the axis of the tube, each alternate plane making an angle of about 60 degrees and 120 degrees with this axis. These planes intersected in parallel straight lines, from each of which stretched a semicircular film to the wall of the glass tube.

A section of the resultant formation is illustrated by the solid model shown in fig. 2, while the formation at the junction R is made clear by the photograph in fig. 1 (Pl. VI.). In this photograph at the point indicated a plane film is about to coalesce with the "chain" system already formed. Photographs of this "chain" system of bubbles are also shown in figs. 2 & 3 (Pl. VI.), the latter being a section as seen from the end of the tube. The bubble tube in these cases was inclined at about 45 degrees to the horizontal, and the character of the bubble system was found to remain unchanged over quite a wide variation of this angle. On a rotation of the bottle B and bubble-tube about the axis of the bubble-tube however, keeping approximately the same angle of inclination, the bubble system was observed to "skew" round (see fig. 4, Pl. VI.) until finally a point was reached

Fig. 2.



where the "chain" system became unstable, and plane films were formed, as shown in figs. 4 & 5 (Pls. VI. & VII.). This definite change of form is apparently dependent upon the size of the air bubbles rising in the liquid. Fig. 5 (Pl. VII.) is of additional interest in that interference fringes may be observed, due to the thinness of the films caused by draining. Fig. 6 (Pl. VII.) shows the formation of the bubbles when the liquid level is above the junction R; in this case the bubbles of air rising through the liquid surface adjust themselves alternately on either side of the tube. Still a further effect was observed on disposing the bubble-tube in a vertical position. A very regular and beautiful "honeycomb" structure was obtained, which is illustrated in fig. 7 (Pl. VII.). In this case the bubble-train consisted of large bubbles each followed by a smaller one (*cf.* Plateau's spherule), this latter having a definite central position in the "honeycomb" structure. They can be observed in the plate as a series of

small plane and nearly rectangular films lying along the axis of the tube.

Experiments were carried out with different liquids in order to test the stability of their bubble systems, if any. Glycerine, acetone, collodion, paraffin, turpentine, Fleuss oil, soap solution, and an aqueous solution of saponin were among the numerous liquids used. Unstable films were obtained in the case of paraffin and turpentine, while the Fleuss oil, soap, and saponin solutions gave films of greater stability. In the plates shown fig. 1 (Pl. VI.) is a soap-film system, fig. 8 (Pl. VII.) was obtained with Fleuss oil, while in each of the remaining cases saponin was used. The photographs were taken with a $f/4{\cdot}5$ reflex camera, and the diffuse lighting was derived from a 100-watt lamp which was "shrouded" by tissue paper. The exposures were of the order of 10 to 20 seconds.

The remarkable flexibility of the saponin-bubbles was investigated by applying an increased external pressure to the chain of the bubbles and observing the compression produced. The change in volume of a given number of the bubbles was found to obey Boyle's Law over a range of 14 cm. of mercury, the range of pressure investigated.

The actual photographs which we have submitted cannot but fail to do full justice to the beauty of the phenomena observed, both from the point of view of the changing interference colours produced by the thinning of the films and also, of the unlimited possibilities of "honeycomb" structure, depending upon the dimensions of the tubes.

XV. *The Photoelectric Effect of Electric Spark Radiation.* *By* John Meiklejohn, *M.A., B.Sc., Research Student in the University of Glasgow* *.

1. THE experiments described in the present paper were carried out with the object of determining by means of a photoelectric photometer how the intensity of the radiation emitted by an electric spark varies with the potential difference of the spark electrodes and with the quantity of electricity discharged in the spark. In the course of the experiments some observations were also made on the sparking potentials of clean and of oxidized spark electrodes, which are thought worthy of placing on record.

* Communicated by Prof. E. Taylor Jones, D.Sc.

The apparatus used in the experiments included an induction coil and a well-insulated spark-gap having a number of pairs of electrodes of different metals which could be conveniently connected in turn with the secondary terminals of the coil. The electrodes were all hemispherical and of the same curvature, being 0·5 cm. in diameter. The sparking potential was measured by an electrostatic voltmeter connected with the spark terminals through a diode valve. The quantity discharged in the spark was indicated by an insulated ballistic galvanometer connected in series with it. The photoelectric effect of the radiations from the spark was measured by a vacuum photoelectric cell (G. E. C., K. M. V. 6) having a potassium layer cathode and a wire mesh anode. The cell was mounted on an insulated stand so that its cathode was 8·5 cm. from the spark-gap, and was entirely surrounded, except for a small window to admit the radiations from the spark, by an earthed metal casing to shield it from external electrostatic effects. The cell, being contained in a thin bulb of glass, was sensitive over the range of the visible spectrum and the ultra-violet from about 2900 to 7000 Å. U.

In the experiments a Leyden jar of about 0·0005 mfd. capacity was connected with the terminals of the spark-gap. This was for the purpose of diminishing the tendency to arcing and of increasing the photoelectric effect.

The cathode of the cell was connected to a quadrant electrometer, by which the total photoelectric emission due to a single discharge could be measured. The deflexion on the electrometer scale could be taken to be proportional to the intensity of the radiation from sparks of different length, since the greatest spark length used was only 1·73 mm. The gap could therefore in all cases be treated as approximately a "point-source."

The interrupter used in the experiments requires special mention. In some preliminary experiments a motor interrupter, giving a rapid succession of sparks, had been tried, but was found unsatisfactory for the following reasons. Owing to the rapid oxidation of the electrodes due to the sparks the current passing in the spark and the radiation from it both diminish rapidly with time after the sparking begins. It is also well known that the potential required to maintain a rapid succession of sparks (once started) is less than that required to produce the first spark.

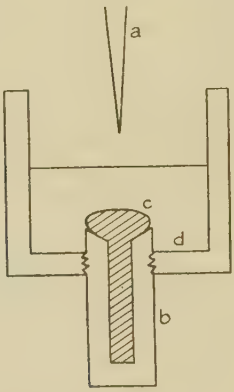
For these reasons, and in order to obtain definite conditions, it was decided to use in the experiments a hand

interrupter just giving single sparks*, and to clean the spark electrode surfaces immediately before each discharge. After each experiment the gap was opened out and the interrupter worked rapidly until the voltmeter reading was constant.

This was taken as the peak voltage of the spark used in the preceding radiation experiment.

The hand interrupter has a new feature, which makes it a distinct improvement upon any of the usual types. Instead of the usual *plane* mercury surface, which is extremely difficult to keep clean in an interrupter, a *convex* surface

Fig. 1.



a=amalgamated copper rod.
b=reservoir screwed into base of cup.
c=mercury contact drop.
d=trap space.

was used—in fact, the surface of a single rather large drop of mercury in a vessel having a concave bed.

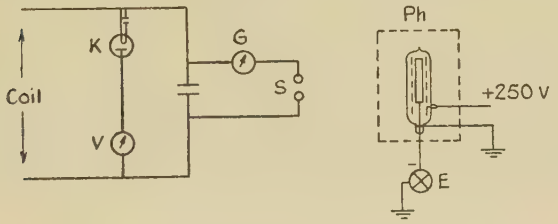
It was noticed that the globules of mercury, mixed with impurities, which form on the mercury surface near the point of contact are unstable at the summit of the convex surface and are easily moved aside so as to leave the surface clean for the next break.

Probably the best form of this new interrupter is that shown in fig. 1, although an effective form is obtained by using a rather deep watch-glass as the container.

* If the primary current is greater than the minimum which gives a spark the discharge takes the form of a multiple spark.

In fig. 2 is shown a general plan of the apparatus.

Fig. 2.



K=diode valve.
V=electrostatic voltmeter.
G=ballistic galvanometer.
S=spark gap.
Ph=photoelectric cell.
E=quadrant electrometer.

Fig. 3.

2. *The Sparking Potentials of Different Metals.*

Figs. 3 and 4 show the curves for different electrode materials when the spark potential is plotted against spark distance.

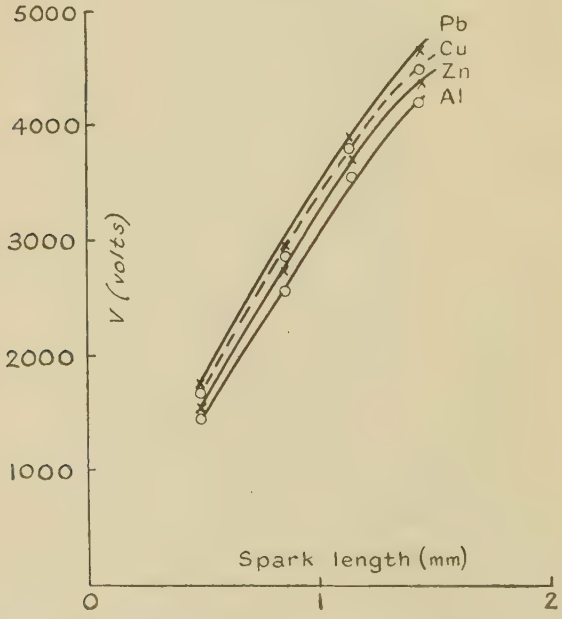
It can be seen that, for a constant spark length, the sparking potential increases according to the following series :—Carbon, bismuth, aluminium, zinc, copper, lead, iron.

Further, the sparking potential V is approximately proportional to the spark length *d*.

Hence $V = Xd$ approximately, so that the electric field strength X is approximately constant for each metal.

There is a distinct difference between the sparking potentials for the different electrode substances, and the

Fig. 4.



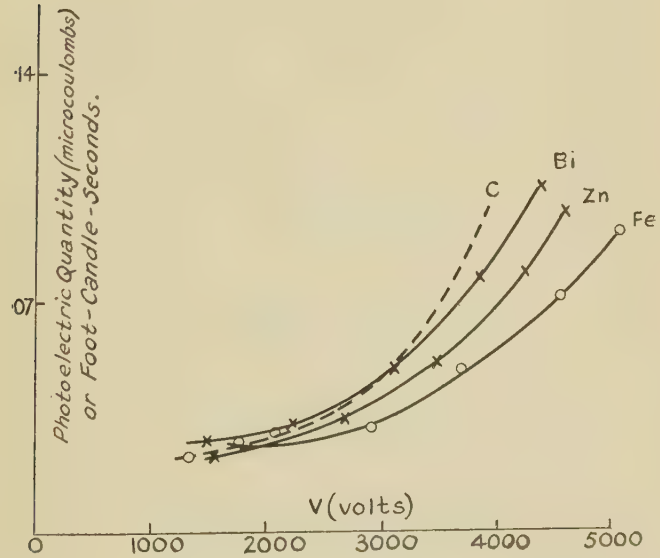
values obtained are lower than those commonly accepted. The explanation is suggested by the observations made on the effect of oxidation of the electrodes at the end of this paper. These tend to confirm the view of J. Taylor ('On the Sparking Potentials of Electric Discharge Tubes') that the nature of the surface plays a part in determining the sparking potential.

In these experiments the sparking surfaces were freshly cleaned immediately before each discharge. The surface layer of impurities and absorbed moisture is thus removed,

at least in part, and this has the effect of increasing the photoelectric emissivity, and making it different for different substances. The increase in emissivity causes a lower potential to be sufficient to yield the number of photoelectrons required to initiate the discharge. In addition, the differences in emissivity of the different substances make different potentials necessary to initiate the discharge.

If the surface layer were not removed by cleaning, the emissivity of this layer would be the same for all the electrodes, so that the same potential would be needed to obtain

Fig. 5.



sufficient photoelectrons to start the discharge. This sparking potential would clearly be greater than that for clean electrodes.

3. *The Relation between Photoelectric Intensity and Sparking Potential.*

The intensity of the photoelectric radiations from a single spark was taken to be proportional to the electrometer charge "e," but the results may also be regarded as being expressed in light units, since it was found that an electrometer charge of 1 micro-coulomb was produced by 1-foot candle in one second.

Figs. 5 and 6 indicate the relation between "e" and V. The shape of the curves suggested the equation $e = aV^2 + bV + c$, and the values of a, b, and c were determined from

Fig. 6.

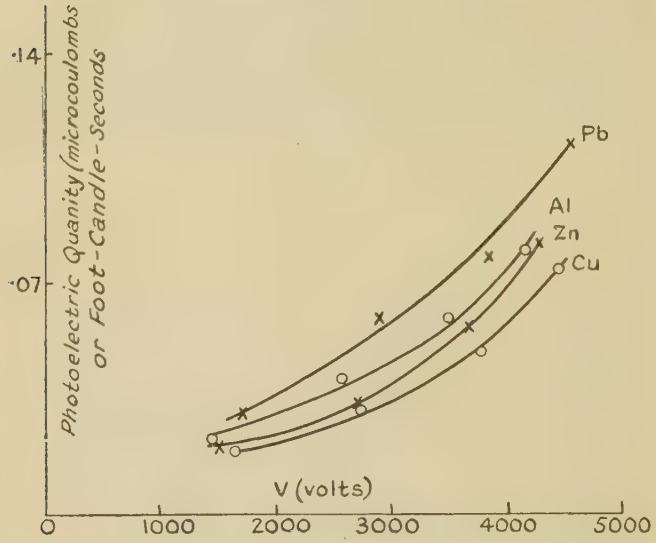


TABLE I.

Electrode Substance.	$a \cdot 10^9$.	$b \cdot 10^6$.	c.	$\frac{b}{a} \cdot 10^{-3}$
Zinc	6·65	−19·3	·036	−2·9
Aluminium	2·8	4·2	·010	1·5
Lead	3·5	3·5	·014	1·0
Copper	5·6	−17·5	·032	−3·1
Zinc	7·7	−25·9	·048	−3·4
Carbon	18·2	−73·5	·104	−4·0
Bismuth.....	10·2	−34·7	·060	−3·4
Iron	4·2	−7·7	·018	−1·8

three points on each curve. The equation was then tested by calculating the values of e for different values of V and comparing with the corresponding observed values. In all cases the differences were negligible, or comparable with the

errors of curve tracing. The values of the constants are shown in Table I.

4. *The Significance of the Relation* $e = aV^2 + bV + c$.

It is supposed that radiation from the gap consists of two components, viz.:—

(1) Radiations accompanying the neutralization of the positive ions at the cathode.

The treatment for this component is obtained from a paper by J. Taylor *. Since the photoelectric cell is only sensitive to a certain range of wave-lengths, only a fraction of this radiation is contributory to e.

It can be shown, if n_0 electrons are produced originally at the cathode by the natural ionizing agents, and $\phi(V, p)$ is a function of the applied voltage and the pressure of the gas, the number of positive ions gathered at the cathode is $n_0[\phi(V, p) - 1]$. Assuming that the neutralization of these ions at the cathode is accompanied by the emission of radiation, some of which falls on the cathode surface and produces the emission of photoelectrons, let the number of these photoelectrons be denoted by $\gamma n_0[\phi(V, p) - 1]$, where γ is some small fraction.

According to this view the intensity of the radiation producing the photoelectric effect is proportional to the number of photoelectrons emitted, so that the intensity of these radiations is $K_3\gamma n_0[\phi(V, p) - 1]$, where K_3 is a constant depending on the substance composing the cathode.

The potential used was just sufficient to initiate the discharge, so that

$$\gamma n_0[\phi(V, p) - 1] = n_0 ;$$

$$\therefore \quad \text{intensity of photoelectric radiations} = K_3 n_0.$$

(2) Radiation from the gas in the gap produced as the result of collisions between ions and neutral molecules. The probability of a collision between an ion and a neutral molecule is proportional to the number of ions present, while the probability of a collision between oppositely charged ions is proportional to the product of the number of positive ions and the number of negative ions. Hence if n is the total number of positive ions, and if the ions of opposite charge are produced in equal numbers,

$$\text{radiation from gas} = K_1 n + K_2 n^2,$$

* "Photoelectric Theory of Sparking Potentials," Proc. Roy. Soc. A, cxvii. p. 508.

where K_1 and K_2 depend on the nature and pressure of the gas.

Hence the total radiation affecting the photoelectric cell is given by

$$e = K_1 n + K_2 n^2 + K_3 n_0. \quad . \quad . \quad . \quad . \quad (A)$$

Since the condenser is assumed to discharge at the moment the spark just appears, *i.e.*, when

$$\gamma n_0 [\phi(V, p) - 1] = n_0,$$

$$n = \frac{n_0}{\gamma} + \frac{CV}{e_1}.$$

But $$\frac{1+\gamma}{\gamma} = \epsilon^{\frac{\alpha V}{X}},$$

where α = number of ions produced by a negative ion in 1 cm. of its path, and e_1 = electronic charge,

or $$\frac{1}{\gamma} \doteqdot \epsilon^{\alpha d} \ldots .$$

since γ is small compared with unity ;

$$\therefore \quad n = n_0 \epsilon^{\alpha d} + \frac{CV}{e_1}.$$

Substituting this value in A, using the relation $V \doteqdot Xd$, and neglecting powers of d above the second, we find

$$e = K_1 n_0 + K_2 n_0^2 + K_3 n_0 + V\left(\frac{K_1 C}{e_1} + \frac{K_1 n_0 \alpha}{X} + \frac{2 n_0 C K_2}{e_1} + 2K_2 n_0^2 \frac{\alpha}{X}\right) + V^2\left(\frac{K_1 n_0 \alpha^2}{2X^2} + K_2 \frac{C^2}{e_1^2} + 2K_2 n_0 \frac{C}{e_1} \cdot \frac{\alpha}{X} + 2K_2 n_0^2 \frac{\alpha^2}{X^2}\right).$$

Comparing with $e = aV^2 + bV + c$, we can write

$$c = K_1 n_0 + K_2 n_0^2 + K_3 n_0,$$

$$b = (K_1 + 2K_2 n_0)\left(\frac{n_0 \alpha}{X} + \frac{C}{e_1}\right),$$

$$a = \frac{K_1 n_0 \alpha^2}{2X^2} + K_2 \left\{ \frac{n_0^2 \alpha^2}{X^2} + \left(\frac{n_0 \alpha}{X} + \frac{C}{e_1}\right)^2 \right\},$$

$$\frac{b}{a} = \frac{2X^2}{n_0 \alpha^2}\left(\frac{n_0 \alpha}{X} + \frac{C}{e_1}\right)\left[1 - \frac{1}{1 + \left(\frac{K_1}{K_2} + 2n_0\right) \times \frac{n_0}{2\left(n_0 + \frac{CX}{e_1 \alpha}\right)^2}}\right].$$

Suppose the applied potential V to be made so small, by diminishing the spark length, that the radiation contribution

(aV^2+bV) is negligible compared with c. Then c is the dominating component of e for all the values of V so obtained. The order in which c varies for different electrodes is seen from Table I. V is supposed to be chosen the same for all the spark-gaps, so we may assume that $K_1+K_2n_0$ is independent of the electrodes used. Variations in c can therefore be attributed to variations in K_3 with the metal. In spite of the difficulties of determining the photoelectric emissivity of substances in air, the variations in c are in general agreement with the differences observed between non-metals and metals. From Table I. it can be seen that $n_0(K_1+K_2n_0)$ is certainly less than ·010. The maximum value of c is obtained with carbon, so that the maximum value of K_3n_0 is greater than ·104—·010, or ·094. For the small values of V indicated the radiation measured is therefore mainly photoelectric radiation produced at the cathode. Further, the order in which this radiation for a given potential diminishes is given by the series C, Bi, Zn, Cu, Fe, Pb, Al. This is the order in which the potential V should increase in order to obtain a self-sustained discharge. This order was found to be given by the series C, Bi, Al, Zn, Cu, Pb, Fe. The only serious exception is Al, for the values for Pb and Fe are not greatly different.

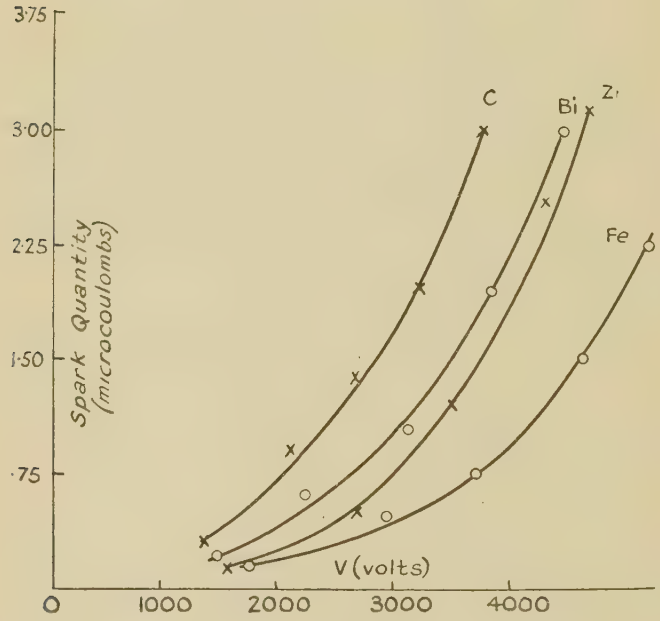
The values of $\frac{b}{a}$ were found to increase along the series C, Bi, Zn, Cu, Fe, Pb, Al. This is the order in which X increases and, consequently, $\frac{1}{\alpha}$ decreases. X does not change much, so for the value of $\frac{b}{a}$ to increase in this order it is necessary that the expression in square brackets should increase more rapidly than $\frac{X^2}{\alpha^2}$ decreases. Hence

$$1+\left(\frac{K_1}{K_2}+2n_0\right)\times\frac{n_0\alpha^2}{2X^2\left(\frac{\alpha n_0}{X}+\frac{C}{e_1}\right)^2}\text{ increases.}$$

The second actor of the product does not change much, so variations in $\frac{b}{a}$ are largely produced by increases in $\frac{K_1}{K_2}$ as we pass along the above series of different electrodes. This is consistent with the large changes observed in the values of b. According, however, to the assumptions made about the production of radiation by collision, K_1 and K_2 should be

constant for a given potential. Apparent changes in K_1 and K_2 may be due to changes in the radiation terms $K_1 n$ and $K_2 n^2$ not accounted for by the indicated changes in n. If additional neutral atoms or molecules were projected into the discharge space, the radiation arising from collision with neutral atoms would increase without any increase in n. This would cause an apparent increase in K_1 in the experiments. Similarly, ionization by collision of the neutral atoms or molecules would lead to an apparent increase in K.

Fig. 7.



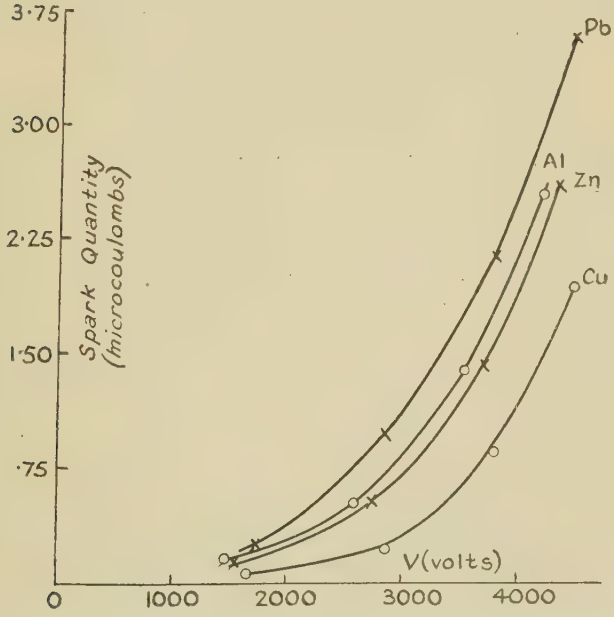
The increase in $\frac{K_1}{K_2}$ can therefore be explained by supposing that neutral atoms or molecules are liberated from the cathode by the bombardment of positive ions. This effect increases along the series C, Bi, Zn, Cu, Fe, Pb, Al. This series does not correlate exactly with the values for melting-point, thermal conductivity, specific heat, or the product of the first with either the second or third. Imperfect correspondence only is obtained, but it must be recalled that metallic particles are probably liberated only from certain points of the electrode surface. Even if the phenomenon

were only a thermal problem the difficulty of allowing for such surface effects complicates the problem greatly.

5. *The Relation between the Quantity of Electricity passing in the Discharge and the Spark Potential.*

The values of Q and V are plotted in figs. 7 and 8, and the equation $Q = AV^2 + BV + C'$ is assumed. The values of the constants are shown in Table II.

Fig. 8.



The divergences of Q from the calculated values were small for the larger values of Q and relatively large for the small values. Considering the errors of curve tracing and the difficulty of measuring accurately small values of Q it was decided that the above equation represented the curve with a considerable degree of accuracy.

When different electrodes are used we see that the constant C′ increases according to the series carbon, Pb, Fe, Zn, Bi, Al, Cu. B decreases according to the series carbon, Pb, Fe, Bi, Zn, Al, Cu. A increases according to the series

Fe, C, Pb, Zn, Cu, Bi, Al, most of the values, however, being nearly the same. $\frac{B}{A}$ increases according to the series carbon, Pb, Bi, Zn, Al, Fe, Cu.

Apart from the serious shift of the pair Pb, Fe, these series agree fairly well with the series already mentioned.

The equation for Q shows that it is not proportional to V, but is a quadratic function of V. The term AV^2 may be explained in the following way:—the spark condition of the discharge rapidly passes into the form of an arc, in which the current is carried by metallic vapour liberated from the cathode by bombardment of positive ions. The amount liberated will be proportional to the energy of the ions for a

Table II.

Electrode substance.	$A \cdot 10^7$.	$B \cdot 10^4$.	C'.	$\frac{B}{A} \cdot 10^{-3}$.
Zinc	3·0	−10·1	1·02	−3·35
Aluminium	3·5	−12.0	1·29	−3·48
Lead	2·9	−6·9	·63	−2·42
Copper	3·0	−12·8	1·43	−4·25
Zinc	3·0	−9·9	1·02	−3·30
Carbon	2·3	−1·5	·17	−·67
Bismuth	3·1	−9·7	1·14	−3·15
Iron	2·0	−7·7	·92	−3·92

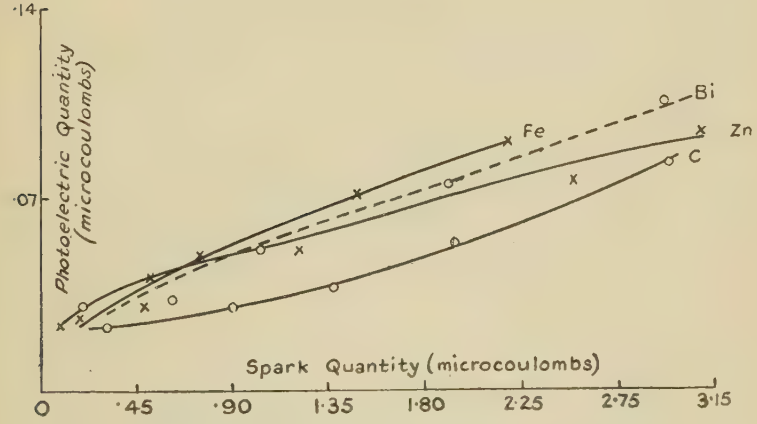
given gas—that is, proportional to V. This effect will contribute a quantity of electricity to the discharge, which is some fraction of the term BV. If the potential is applied for a sufficient time the atoms of the metal will become ionized, the ionization potential of the metal being lower than that of the gas, and will thus yield additional positive ions. These bombard the cathode and liberate additional atoms and molecules of the metal. The number of these additional carriers is therefore proportional to $V \times V$. This process is cumulative and is only limited by the time of application of the potential and the power available. The effect would be shown by the addition of V terms of higher order to the equation for Q. The equation obtained shows that the potential has only been applied long enough to secure a term in V^2.

These considerations explain the changes in A and B with the electrodes used, but the series do not follow exactly any definite law. The fact that the emission of metallic vapour takes place from certain points of the surface only makes the discovery of such a law difficult.

6. *The Relation between Photoelectric Intensity and the Quantity of Electricity passing in the Discharge.*

Figs. 9 and 10 show the $e-Q$ curves. It can be seen that these parabolic curves do not differ much from straight lines over most of the range.

Fig. 9.



Putting $c-e=d$ and $C-Q=q$ in the equations

$$aV^2+bV+c-e=0,$$

$$AV^2+BV+C-Q=0,$$

and eliminating V^2 and V, we find $(Ad-aq)^2=(Bd-bq)(Ab-aB)$. By neglecting small values of the coefficients the approximate equation for the curves when q is not very small or large becomes $A^2d=2Aaq+B(Ab-aB)$. The shapes of the various curves are explained when the values of the constants are substituted. The equation for the curve for carbon is, approximately, $e=\cdot16Q+\cdot038$. For a given value of Q the value of e increases along the series C, Zn, Al, Bi, Cu, Pb, Fe.

The graphs, being approximately straight lines, show that the radiation is mainly arc radiation.

7. *The Relation between e and the Product* QV.

If QV = E, the energy in the spark, the equation for E becomes

$$E\{a^2bc-2abAd+a^2Bd-b^2(aB-Ab)\}$$
$$=d\{(aC-Ad)^2-(aB-Ab)(bC-Bd)\}$$

Fig. 10.

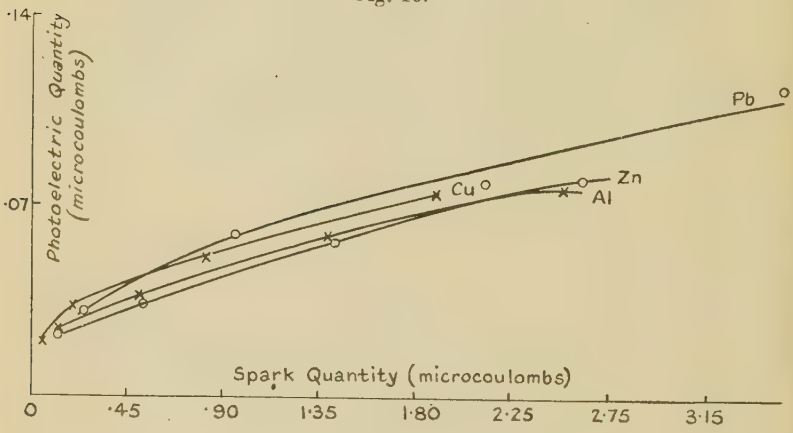
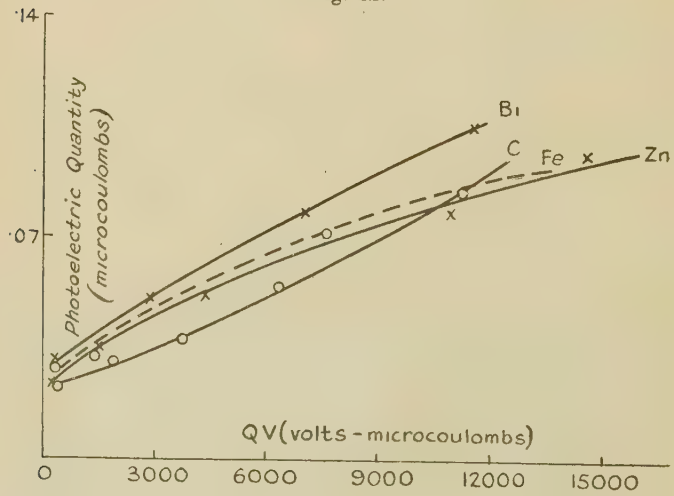


Fig. 11.



or, approximately,

$$E\{a^2bc-b^2(aB-Ab)\}$$
$$=d\{(aC-Ad)^2-(aB-Ab)(bC-Bd)\}.$$

E is therefore a cubic function of e, but the graphs do not differ much from straight lines. This is especially the case for carbon. Hence e is approximately a linear function of QV, *i.e.*, the photoelectric intensity is proportional to the energy of the spark and varies with the electrodes used.

8. *Additional Observations: The Effect of Oxide on the Spark Potential.*

When the minimum spark potential had produced a discharge between freshly cleaned electrodes no additional

Fig. 12.

discharge could be obtained: an increase of potential was necessary. An attempt was made to investigate this quantitatively. The electrodes were cleaned, and the minimum spark potential was measured. The potential was then increased from a low value until a second spark was obtained. This procedure was repeated, and the values of the potential were plotted against abscissæ representing the number of the spark, since it is reasonable to assume that the oxidation of the surfaces is proportional to the number of the spark if the number is small.

With rare exceptions it was found that the first three or four points lay on a straight line, and further points showed a more or less steady increase of the potential. Preliminary

experiments showed, however, that the probability of obtaining a second or third spark at a certain potential increased as this procedure was carried out. This may be due to the nearest clean portions of the electrodes (surrounding the oxidized parts) now occupying a larger area of the electrode surfaces. Some typical examples are given in Table III.

It can be seen that the spark potential can be taken as a linear function of the oxidation for the first three sparks. The observations on the effect of oxidation are in agreement with those on the effect of exposing clean surfaces to the air for various long periods. It should be noted that the effect

TABLE III.

Spark Potentials (volts).

Number of spark.	Zinc spheres. Diameter = ·2 cm.		Carbon hemispheres. Diameter = ·5 cm.
	Spark length = ·5 mm.	Spark lengt. = 1·0 mm	Spark length = 1·3 mm.
1	1580	3210	3060
2	1890	3500	3170
3	2160	3820	3310
4	2350	4050	3260
5	2420	4650	3330
6	—	4700	3270

is small in the case of carbon, presumably because this does not tarnish or oxidize easily.

The amount of oxide produced by a spark was so small as to cause only a slight dulling of the surface, yet this is sufficient to alter the spark potential considerably. The oxidation would produce a considerable reduction in the photoelectric emissivity of the surface. In order to obtain sufficient energy from the photoelectrons to produce ionization by collision to enable the second spark to pass it would be necessary to increase the applied potential.

These observations are not new, but serve to confirm the necessity of considering the nature and state of the electrode surfaces, as is done in the Photoelectric Theory of Sparking Potentials.

Summary.

The results obtained indicate that the intensity of the photoelectric radiation and the quantity of electricity discharged from single sparks were both quadratic functions of the minimum sparking potential. These three quantities depend on the physical and chemical nature of the electrodes used. The variations in the quantities for electrodes of the same shape follow the order, carbon, bismuth, aluminium, zinc, copper, lead, iron, with certain exceptions. The effect of the electrode substance tends to confirm the photoelectric theory of sparking potentials. The variations are also probably dependent on vapour liberated into the discharge from the electrodes. It was found also that the intensity of the photoelectric radiation was approximately a linear function of the quantity of electricity discharged and also of the energy of the spark. Here, again, the results varied with the electrode substance. Experiments on the effect of oxide on the sparking potential showed that surface conditions play a part in determining the sparking potential.

In conclusion, the author wishes to express his gratitude to Prof. Taylor Jones for his kind and invaluable assistance, and also to Dr. John Thomson for some useful suggestions. This work was performed in the Research Laboratories of the Natural Philosophy Department of Glasgow University.

XVI. *The Calculation of Surface Tension from Experiment.*—Part I. *Sessile Drops.* *By* ALFRED W. PORTER, *D.Sc.*, *F.R.S.*, *Emeritus Professor of Physics in the University of London* *.

THE calculation of surface tension from measurements of sessile drops or from ascension in capillary tubes may be summarized in the equation

$$\beta\left(\frac{1}{R_1}+\frac{1}{r}\right)=\frac{h_0+h}{\beta},$$

where β^2 is the capillary constant $\sigma/g\rho$, h is the height from the mid-point of the surface to the plane of greatest section, r is the radius of this section, R_1 the first radius of curvature of the surface where it meets this section, and h_0 is the capillary elevation at the midpoint (and determines the curvature at this point). Diagram fig. 1 A shows the sessile

* Communicated by the Author.

drop and fig. 1 B the case of the ascent in a capillary tube. The equation is written in a non-dimensional form.

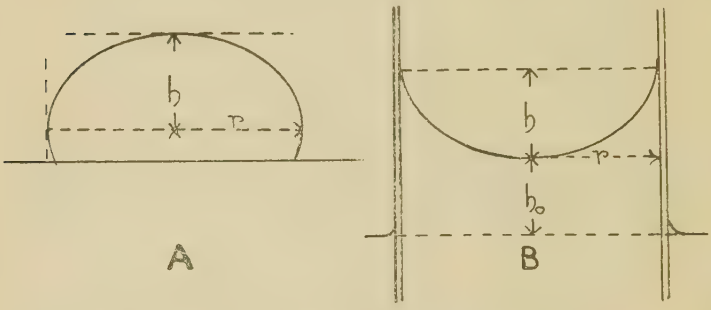
In the case of a capillary tube h_0/β is an important magnitude, while h/β is an unwanted complication which vanishes if the tube-radius is vanishingly small. In the case of large sessile drops h/β is the important magnitude, whereas h_0/β is often insignificant.

Intermediate cases exist in which both terms require consideration.

Sessile Drops.

It is recognized that no simple formula is to be expected except for very large drops. The measurements usually made are h and r (fig. 1 A). Formulæ have been given by Worthington (Phil. Mag. 1885), Allan Ferguson (Phil. Mag.

Fig. 1.



1913), and by the third Lord Rayleigh (Proc. Roy. Soc. A, xcii. p. 184 (1915)). Worthington's formula is equivalent to

$$\frac{\beta^2}{r^2} = \frac{\frac{1}{2}\frac{h^2}{r^2}}{\left(1+\cdot 609\frac{h}{r}\right)}.$$

Ferguson's is equivalent to

$$\frac{2\beta^2}{r^2} = \frac{h^2}{r^2} - \cdot 609\left(\frac{2\beta^2}{r^2}\right)^{3/2},$$

in which he writes a_1^2 instead of $2\beta^2$, in the continental fashion. This equation has to be solved by successive approximations ; the process is made simpler if we write

$$\frac{2\beta^2}{r^2} = \frac{\frac{h^2}{r^2}}{\left(1+\cdot 609\left(\frac{2\beta^2}{r^2}\right)^{1/2}\right)},$$

which at the same time brings out its resemblance to and difference from Worthington's formula. Rayleigh obtains one equivalent to

$$\frac{h}{\beta}=\sqrt{2}+\cdot 6095\frac{\beta}{r},$$

from which a very similar formula can be deduced. In each case the curvature at the mid-point is neglected, though it is recognized that except for very large drops some allowance for it is necessary. Unfortunately no indication is given as to the size of drop which may be considered a large one, and these formulæ are still hopefully used by experimentalists for drops of medium size.

For large drops Rayleigh (*loc. cit.*) showed how the curvature at the mid-point can be calculated, and obtained

Table I.

$\frac{r}{\beta}$.	$\frac{h_0}{\beta}$.
6	·0149
7	·0059
8	·0023
9	·00089
10	·00034

the following values. The table can be easily extended to include higher values of r/β ; for example, for

$$\frac{r}{\beta}=20, \quad \frac{h_0}{\beta}=2\cdot 04\times 10^{-8}.$$

By means of these an approximate correction for this curvature can be applied to the values given by his simple formula. This correction is needed for values of h^2/r^2 as low as 0·03.

Besides these determinations there is the table drawn up by A. Heydweiller (*Ann. d. Phys.* lxv. p. 311 (1898)), based largely upon the formulæ of T. Lohnstein (*Wied. Ann.* liii. p. 1062 (1894) ; liv. p. 713 (1895)). This table is the most complete one published up to the present. The values given appear, however, to be too low even in the case of very large drops. Lohnstein gave two formulæ for β/h, one yielding

a maximum the other a minimum value. These formulæ give results differing sometimes by close on 3 per cent. for β/r; this would mean nearly 6 per cent. on β^2/r^2 (or σ). Since Heydweiller takes the arithmetic mean of these extremes, a wide range of uncertainty is introduced, which may account for his tabulated values being too low. In fact, if the arithmetic mean of β^2/r^2 is taken instead of the arithmetic mean of β/h, the values come very much closer to those derived in this paper by a totally different method (not involving maxima and minima). For example, take the important case of $h^2/r^2 = 0{\cdot}16$, for which the value is most uncertain. We have

Value based on mean β/h	·07235 (Heydweiller)
Value based on mean β^2/r^2 ...	·07289
Value derived in this paper ...	·07295

The only conclusion that can be arrived at is that the extreme values are too far apart for any arbitrarily selected kind of mean to be reliable.

These remarks apply to large drops.

On the other hand, drops of water of *less* than ·87 cm. radius and of mercury of *less* than ·6 cm. (in both cases ordinary temperatures being assumed) come within the scope of Bashforth and Adams's tables, and these may be put in such a form that very exact calculations of surface tension can be made from experimental data. The transformations necessary appear never to have been made in such a way as to bring out certain important properties, which are consequently not emphasized.

For example, for *very large* drops the simple formulæ give

$$\frac{\beta^2}{r^2} = \frac{1}{2}\frac{h^2}{r^2}.$$

It does not appear to have been noticed that for drops of mercury of about 0·5 cm. radius this is once more true! A little calculation based on the tables shows that it is the case. The standard values in Table II. based on B. and A. tables enable the fact to be elicited.

These values take into account the precise shape of the drop and are considered as being accurate to about five significant figures.

Even without the tables the existence of a point of zero correction can be demonstrated. When the radius is very large $\beta^2/r^2 < \frac{1}{2}h^2/r^2$; when the radius is very small $\beta^2/r^2 \to \infty$,

while $h^2/r \to 1$, and the intervening changes are continuous; so that β^2/r^2 is then the greater *.

There remain the calculations of β^2/r^2 for intermediate values of h^2/r^2. These can best be obtained by plotting the values obtained from Bashforth and Adams and those from Rayleigh (corrected for curvature at the mid-point) on a diagram of r/β against r/h. The intervening gap can be safely filled in by a curve having slight curvature, taking care that the drawing-curve employed shall fit simultaneously two or three points of the previously ascertained values at each end of the gap. By repeating the process assurance

TABLE II.

$\frac{h^2}{r^2}$.	$\frac{\beta^2}{r^2} - \frac{1}{2}\frac{h^2}{r^2}$.	$\frac{\beta^2}{r^2}$.
·948341	+7·8485	$8·3227_2$
·905923	$3·8606_0$	$4·3135_6$
·839539	$1·8788_3$	$2·2986_9$
·789864	1·22456	$1·6194_9$
·750063	·90091	$1·2759_4$
·538453	$·19466_3$	$·4638_9$
·426071	$·07331_4$	$·2863_5$
·358633	$·03326_3$	$·2125_9$
·313675	$·01570_9$	$·1725_5$
·281426	$·00666_8$	$·1473_8$
·257040	$+·00153_8$	$·1300_6$
·237900	$-·00161_3$	$·1173_4$
·209567	$-·00492_9$	$·0998_5$

was obtained that values of considerable accuracy could be obtained in this way. A diagram was then made extending from $h^2/r^2 = 0$ to $h^2/r^2 = \frac{1}{4}$, showing the difference Δ between β^2/r^2 and $\frac{1}{2}\,h^2/r^2$. This diagram just includes the point at which Δ equals zero, viz., $h^2/r^2 = \frac{1}{4}$ (as shown by aid of B. and A.). An equation was then fitted to this difference curve. It was found that the equation

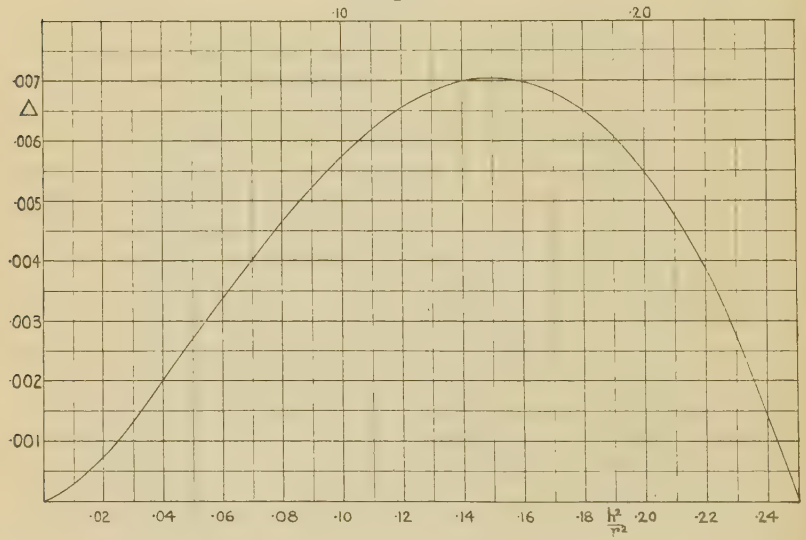
$$\Delta = ·3047\frac{h^3}{r^3}\left(1 - 4\frac{h^2}{r^2}\right)$$

* While this paper is in the press a paper has been published by R. S. Burdon (Farad. Soc. p. 869, December 1932), in which he states that a student of his has lately shown by experiment that such a point exists.

fits, *as perfectly as could be determined*, the values that had been obtained by the several methods throughout the whole of this diagram. The curve is shown in fig. 2. In framing the equation recognition has been made of the existence of a point at which Δ vanishes. Not only does it vanish there, but the curve has the right slope on approaching this point, as indicated by the tables. It must be noted that, in calculating β^2/r^2, Δ is subtractive throughout the extent of the diagram.

The values calculated are shown also in the accompanying Table III., which also includes a few values calculated from

Fig. 2.



Ferguson's and Worthington's formulæ, in order to indicate the range in which these are sufficiently accurate. The last column gives the approximate radius r of a mercury drop which corresponds.

Some remarks are necessary upon the reliability of the sessile drop method for determining surface tensions. For large drops ($h^2/r^2 = \cdot 01$) the correcting term Δ is 5 per cent. of the principal term, but is safely known. It is doubtful if the final value of σ can be trusted to much less than 1 per cent. When $h^2/r^2 = \cdot 05$, Δ is responsible for 10 per cent., and is fairly safely known. When $h^2/r^2 = \cdot 20$ the percentage drops to about 5, and at ·25 it drops to zero, and

is in that neighbourhood known with great certainty from B. and A. It would seem that the last case is the most desirable of any to aim at*. For mercury it implies a radius

TABLE III.

$\frac{h^2}{r^2}$.	$\frac{1}{2}\frac{h^2}{r^2}$.	Subtractive Δ.	$\frac{\beta^2}{r^2}$.	Ferguson.	Worthington.	r radius of mercury drop (approx.).
·01	·005	·00029	·00471			cm.
·02	·01	·00078	·00922	·00922	·00921	2
·03	·015	·00139	·01361			
·04	·02	205	·01795	·0179	...	1·4
·05	·025	272	·02228			
·06	·03	337	·02663			
·07	·035	404	·03096			
·08	·04	466	·03534	...	...	1
·09	·045	526	·03974			
·10	·05	·00578	·04422	·0425	·0420	
·11	·055	622	·04878			
·12	·06	657	·05343			
·13	·065	680	·05820			
14	·07	697	·06303			
·15	·075	707	·06793	·0618	·0607	0·7
·16	·08	702	·07295			
·17	·085	680	·07820			
·18	·09	650	·08250			
·19	·095	603	·08897			
·20	·10	·00550	·09450	·0804	·0785	
·21	·105	475	·10025	...	...	0·6
22	·11	390	·1061			
23	·115	280	·1122			
·24	·12	149	·1185			
·25	·125	0	·125	·0980	·0958	0·54

of about 0·54 cm. Most uncertainty as to the true value of Δ appertains to values of h^2/r^2 between 0·08 and 0·18.

* Quincke's experiment on mercury for the case $h^2/r^2 = 0{\cdot}217$ (*i. e.*, $r = 0{\cdot}6$ cm.) when reduced in the way here described gives σ within 1 part in 700 of the value obtained by the capillary tube method.

Verschaffelt has declared against measurements using large drops ("a really practical importance cannot be ascribed to them"). It would seem, however, that with judgment they may be employed successfully. This is satisfactory, because in some cases this method is the only one available.

XVII. *Extension of the Methods of Heaviside's Calculus in Calculation of Circuits containing Parameters varying with Time. By* JACOB NEUFELD, *Cornell University, Ithaca, N.Y.* *

THE problem treated in the following paper consists in finding the current resulting from the application of an e.m.f. varying according to a given law $E(t)$ to an electrical circuit whose parameters are varying explicitly with time. A varying electrical circuit may be expressed analytically by a hybrid operational expression $f(pt)$ [containing the time variable t and the operator $p = \frac{d}{dt}$] and which determines the operational expression for the admittance of the circuit at any moment t. It must be recognized that the function $f(pt)$ expressing the law according to which the parameters vary does not completely determine the solution. It is necessary to state in addition the mechanism according to which this variation is affected and which determines the law governing the phenomena. As an example, we may consider a coil which for the values of time $t < t$, has an inductance L_1 and for $t > t$, L_2. This sudden change may be effected, for instance, by a collapse of the coil or by a sudden insertion of an additional coil in parallel. In the first case an infinite voltage will be induced in the coil according to the formula: $L\frac{di}{dt} + i\frac{dL}{dt} = e$ (term $\frac{dL}{dt}$ is infinite). In the second case, however, the electrical process is entirely continuous and the above formula is not valid for the composite circuit.

In treating the problem of variable parameters we may distinguish two mechanisms of variation which we shall designate by Type I. † and Type II. Each of these types will

* Communicated by the Author.

† For discussion of variable electrical systems of Type I. see J. R. Carson, "Theory and Calculation of Variable Electric Systems," Phys. Rev. xvii. p. 116 (1921).

give a totally different solution for the response of the circuit varying according to the law $f(pt) = \frac{1}{Z(pt)}$ and subjected to a "unit" e.m.f.

Type I.—The variation of the circuit may be effected in a manner equivalent to a continuous insertion of infinitesimal increments of impedance in series according to the law $Z(pt)$. The phenomenon can then be described analytically by a differential equation of the type $Z(pt)i=1$, which, for instance, in case of a variable inductance in series with a variable resistance takes the form :

$$Z(pt)i \equiv L\frac{di}{dt} + i\frac{dL}{dt} + Ri = 1.$$

Type II.—The variation of the circuit may be effected in a manner equivalent to the continuous insertion of infinitesimal increments of admittance in parallel according to the law $f(pt) = \frac{1}{Z(pt)}$.

The treatment presented in this paper will be limited to the type II. of variation of the circuit parameters. It is based on Boltzmann's principle of superposition, stating that the total effect of simultaneously applied causes may be obtained by adding the effects of each acting independently. In our particular case the principle of superposition presents itself in two different aspects which we shall designate by letters A and B.

Principle A, usually applied to circuit problems with fixed parameters, states that if several sources of e.m.f. act in the same network, they will produce a current which will be the sum of the currents produced by each e.m.f. acting alone.

Principle B refers to a circuit subjected to a unit electromotive force at time $t = 0$. It states that if the operational admittance $\frac{1}{Z(p)}$ of the circuit is $f(p) = f_1(p) + f_2(p)$ then the indicial admittance of this circuit will be

$$A(t) = A_1(t) + A_2(t),$$

where

$$A_1(t) = f_1(p)\,1 \qquad \text{and} \qquad A(t) = f(p)\,1.$$
$$A_2(t) = f_2(p)\,1$$

It is logical to assume that if the operators $f_1(p)$ and $f_2(p)$ are applied at different times their effects will add. Consider, for instance, a circuit of operational driving point admittance $t_1(p)$ and which at time $t = \lambda$ changes suddenly its characteristics. We may represent this discontinuous change as an insertion of an additional driving point admittance $\Delta_1(p)$ in parallel. The response of the circuit will then be

$$A(t) = A_1(t) + \Delta A_1(t-\lambda)$$

or

$$F(p) = f_1(p) + \Delta f_1(p) e^{-\lambda p},$$

where

$$A_1(t) = f_1(p)\,1 \qquad \text{and} \qquad \Delta A_1(t) = \Delta f_1(p)\,1.$$

The above considerations may be generalized to a circuit with parameters varying discontinuously according to a step function, that is, when to the operational admittance $f(p)$ there are added increments $\Delta_1 f_1(p)$, $\Delta_2 f_1(p)$, $\Delta_3 f_1(p)$ ... at times $\lambda_1, \lambda_2, \lambda_3 \ldots$, the corresponding indicial admittance is as follows:

$$F(p) = f_1(p) + \Delta_1 f_1(p) e^{-\lambda_1 p} + \Delta_2 f_1(p) e^{-\lambda_2 p} + \Delta_3 f_1(p) e^{-\lambda_3 p} + \ldots$$

or

$$A(t) = A_1(t) + \Delta_1 A_1(t-\lambda) + \Delta_2 A_1(t-\lambda_2) + \Delta_3 A_1(t-\lambda_3) \ldots .$$

Let us assume that the times $\lambda_1, \lambda_2, \lambda_3 \ldots$ lie closer and closer and that the variations of the circuit characteristics are of the same order of magnitude that the intervals $\lambda_n - \lambda_{n-1} = \Delta\lambda_n$.

It is natural to assume that the principle of superposition will hold also in limiting case of

$$A'(t) = \lim_{\Delta\lambda_n \to 0} \left[A_1(t) + \sum_1^n \Delta A(t-\lambda_n) \right].$$

This expression becomes a definite integral which under ordinary circumstances is very difficult to evaluate.

It will be seen later that we are quite justified in considering the operational equivalent of the function $A'(t)$ as

$$F'(p) = \lim_{\Delta\lambda_n \to 0} \left[f(p) + \sum_1^n \Delta_n f(p) e^{-\lambda_n p} \right]$$

and that in evaluation of this expression we can proceed by ordinary integration, the operator p being considered as an ordinary algebraic coefficient. In order to establish this relation, the following theorem is necessary:

THEOREM.

Let the relation

$$f(p\lambda)\,1 = \mathrm{H}(t\lambda) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

be satisfied for any real value of λ bounded within the interval a–b. It follows then that

$$\int_a^b f\,(p\lambda)\,d\lambda 1 = \int_a^b \mathrm{H}(t\lambda)\,d\lambda. \quad . \quad . \quad . \quad (2)$$

Suppose the interval a–b to be subdivided by the insertion between a and b of the intermediate points $\lambda_1\lambda_2 \ldots \lambda_{n-1}$.

Let us form the sum

$$S = (\lambda_1-\lambda_0)f(p\xi_1) + (\lambda_2-\lambda_1)\,f(p\xi_2) + \ldots$$

$$+ (\lambda_n-\lambda_{n-1})f\,(p\xi_n = \sum_1^n f\,(p\xi_k)\Delta_k\lambda, \quad . \quad (3)$$

where ξ_k is any point in the interval $\Delta_k\lambda$.

Formula (3) represents an operational expression which, on account of the relation (1) is equivalent to the following analytical functions:

$$(\lambda_1-\lambda_0)\mathrm{H}(t\xi_1) + (\lambda_2-\lambda_1)\,\mathrm{H}(t\xi_2) + \ldots$$

$$+ (\lambda_k-\lambda_{n-1})\mathrm{H}(t\xi_n) = \sum_1^n \mathrm{H}(t\xi_k)\Delta_k).$$

From the relation

$$\sum_1^n f(p\xi_k)\Delta_k\lambda\,1 = \sum_1^n \mathrm{H}(t\xi_k)\Delta_k\lambda$$

follows

$$\frac{1}{p}\sum_1^n f\,(p\xi_k)\Delta_k\lambda) = \int_0^\infty e^{-pt}\Big[\sum_1^n \mathrm{H}\,(t\xi_k)\Delta_k\lambda\Big]dt$$

or

$$\frac{1}{p}\sum_1^n f\,(p\xi_k)\Delta_k\lambda) = \sum_1^n \Delta_k\lambda \int_0^\infty e^{-pt}\mathrm{H}(t\xi_k)\,dt. \quad . \quad (4)$$

Let us call Δ the greatest of $\Delta_k\lambda$'s. As Δ approaches zero n becomes infinite and both sides of the expression tend to the following limits:

$$\frac{1}{p}\int_a^b f(p\lambda)\,d\lambda = \int_a^b d\lambda \int_0^\infty e^{-pt}\mathrm{H}(t\lambda)\,dt.$$

On account of the uniform convergence of the infinite integral in the above expression we can put it in the following form:

$$\frac{1}{p}\int_a^b f\,(p\lambda)\,d\lambda = \int_0^\infty e^{-pt}dt\int_a^b \mathrm{H}(t\lambda)\,d\lambda. \quad . \quad . \quad (5)$$

The expression (5) is a Carson's infinite integral corresponding to the following relation :

$$\int_a^b f(p\lambda)d\lambda\, 1 = \int_a^b \mathrm{H}(t\lambda)d\lambda,$$

which was to be proved.

Let us now consider a network whose parameters vary continuously with time. Its operational admittance will contain the variable λ and will be represented by

$$f(p\lambda) = \frac{1}{\mathrm{Z}(p\lambda)}.$$

The approximate result can be obtained by finding the effect of a step function which closely fits the function $f(p\lambda)$ so that the indicial admittance is considered as a sum of the term due to $f(p0)$ applied at $\lambda=0$ plus a lot of similar but smaller jumps due to terms $\Delta_k f(p) = \frac{d}{d\lambda} f(p\lambda_k)\Delta_k\lambda$ occurring at times $\lambda_1\lambda_2 \ldots \lambda_k$.

The corresponding result will be then

$$\mathrm{F}(p) = f(p0) + \Sigma e^{-\lambda_k p} \frac{d}{d\lambda} f(p\lambda_k)\Delta_k\lambda,$$

and in case of a continuously varying circuit

$$\mathrm{F}'(pt_1) = f(p0) + \int_0^b \left[\frac{d}{d\lambda} f(p\lambda)\right] e^{-\lambda p} d\lambda, \quad . \quad . \quad (6)$$

where t_1 is the period of time during which the parameters of the circuit have varied.

The operational expression $\mathrm{F}'(pt_1)$ can be computed according to the usual Heaviside's methods (t_1 is constant), and it gives the response of a varying circuit to a unit e.m.f. for any time $\lambda \geq t_1$.

It is assumed also that the characteristics of the circuit vary according to the law $f(p\lambda)$ during the period $0 < \lambda < t_1$, whereas for $\lambda > t_1$ they are constant and the operational admittance is $f(pt_1)$. The operational expression (6) is defined by the following integral relation :

$$\frac{\mathrm{F}'(pt_1)}{p} = \int_0^\infty e^{-pt} \mathrm{A}'(tt_1)dt.$$

Since this expression is satisfied for any value of t_1 and since we are interested mainly in $t = t_1$ we can extend the

meaning of the expression (6) by putting instead of the relation

$$F'(pt_1)\,1 = A'(tt_1)$$

the following

$$F'(pt)\,1 = A'(tt) = B(t),$$

where $B(t)$ represents the admittance of a varying circuit (according to the law $f(pt)$ for any moment t).

It is understood that the operational expression $F'(pt_1)$ is to be computed according to the usual rules (expansion theorem, convergent or divergent series), while p is considered as an operator and t entering in the expression is to be considered as an algebraic coefficient.

The expression (6) can be represented in a more compact form

$$F'(pt_1) = \int_0^{t_1} pf(p\lambda)e^{-\lambda p}d\lambda. \quad . \quad . \quad . \quad . \quad (7)$$

In fact, integrating by parts, we obtain

$$F'(pt_1) = \left[\frac{pe^{-\lambda p}f(p\lambda)}{-p}\right]_0^{t_1} + \int_6^{t_1} e^{-\lambda p}\frac{d}{d\lambda}f(p\lambda)d\lambda$$

$$= f(p0) - f(pt_1)e^{-t_1 p} + \int_0^{t_1} e^{-\lambda p}\frac{d}{d\lambda}f(p\lambda)d\lambda.$$

In the above expression the term $f(pt_1)e^{-t_1 p}$ represents a function of the time shifted a distance t_1 on the time axis and, in the case of a non impulsive network, equalling zero for $t < t_1$. Since, as we stated before, we are interested only in $t = t_1$ the term $f(pt_1)e^{-t_1 p}$ may be eliminated and the expression (7) becomes identical to (6) and the relation

$$F'(pt_1) = \int_0^{t_1} pf(p\lambda)e^{-\lambda p}d\lambda$$

is established.

By performing successive integrations by parts the expression may be put in the following form :

$$F'(pt_1) = \left\{ -e^{-\lambda p}\left[f(p\lambda) + \frac{1}{p}\frac{d}{d\lambda}f(p\lambda) + \frac{1}{p^2}\frac{d^2}{d\lambda^2}f(p\lambda) + \ldots\right]\right\}_0^{t_1}$$

$$= \left[f(p0) + \frac{1}{p}\frac{d}{d\lambda}f(p0)\,\frac{1}{p^2}\frac{d^2}{d\lambda^2}f(p0) + \ldots\right] - e^{-t_1 p}\left[f(pt_1) + \frac{1}{p}\frac{d}{d\lambda}f(pt_1) + \ldots\right].$$

Since we are interested in $t = t_1$ the second term of this expression (representing a function shifted a distance t_1 along the time axis) may be eliminated, and the expression (7) then takes the following form :

$$\phi(p0) = f(p0) + \frac{1}{p}\frac{d}{d\lambda}f(p0) + \frac{1}{p^2}\frac{d^2}{d\lambda^2}f(p0) + \ldots . \qquad (8)$$

The expressions (7) and (8) give the response of a varying circuit to a unit e.m.f. applied at time $t = 0$. If the unit e.m.f. be applied at any other instant $t = \lambda_1$, the corresponding expression for the response will be

$$\phi(p\lambda_1) = f(p\lambda_1) + \frac{1}{p}\frac{d}{d\lambda}f(p\lambda_1) + \frac{1}{p^2}\frac{d^2}{d\lambda^2}f(p\lambda_1) + \ldots .$$

It is understood that the above expression is zero for $t < \lambda$.

Let $$\phi(p\lambda_1)1 = A_v(t\lambda_1).$$

The function $A_v(t\lambda_1)$ represents the indicial admittance of the varying circuit. It is to be noted that in the case of a circuit with constant parameters the indicial admittance is a function of t only, and is totally independent of the instant at which the unit e.m.f. was applied to the circuit. However, in case of a circuit with varying parameters the indicial admittance $A_v(t\lambda_1)$ is expressed as a function of the independent time variable t, and of the instant λ_1 of application of the unit e.m.f.

It was shown by M. F. Gardner* that the principle of superposition A holds also for circuits varying with time.

If $A_v(t\lambda_1)$ is the indicial admittance of the varying circuit and $E(\lambda_1)$ is the e.m.f. applied to the circuit, then the corresponding current at an instant t' will be

$$I = E(0)A_1(t0) + \int_0^{t'} A_v(t - \lambda_1\lambda_1)\frac{dE(\lambda_1)}{d\lambda_1}d\lambda_1$$

or

$$I = \left[\phi(p0)E(0) + \int_0^{t'} \phi(p\lambda_1)\frac{dE(\lambda_1)}{d\lambda_1}d\lambda_1\right]1.$$

It will be of interest also to treat this problem without the use of Heaviside's Calculus. Consider, for instance, a circuit of varying impedance $Z(p\lambda)$ energized by a varying e.m.f. $E(\lambda)$. We may define as generalized indicial

* Transactions of A.I.E.E. xlviii. p. 719 (1929).

admittance an expression which satisfies the operational relation : $N(t\lambda) = \frac{1}{Z(p\lambda)}$ for any value of λ. The expression $N(t\lambda)$ is usually a solution of a linear differential equation with constant coefficients.

Due to the principle of superposition B the indicial admittance of the varying circuit (corresponding to the instant of application of the unit e.m.f. $t = 0$) takes the following form :

$$A_v(t0) = N(t0) + \int_0^t \frac{d}{d\lambda} N(t-\lambda_1\lambda)d\lambda.$$

If the unit e.m.f. is applied at any other instant $t = \lambda_1$ the corresponding expression of the indicial admittance is

$$A_v(t\lambda_1) = N(t\lambda_1) + \int_{\lambda_1}^t \frac{d}{d\lambda} N(t-\lambda_1\lambda)d\lambda$$

and on account of the principle of superposition A, the resulting current will take the following form :

$$I(t) = E(0)A_v(t0) + \int_0^t A_v(t-\lambda_1\lambda_1)\frac{dE(\lambda_1)}{d\lambda_1}d\lambda_1.$$

In conclusion I wish to express my gratitude to Mr. J. R. Carson, of the American Telephone and Telegraph Co., and to Prof. E. H. Kennard, Cornell University, for their valuable suggestions.

XVIII. *Radiation in Gaseous Explosions.* *By* Prof. W. T. David, *Sc.D., and* R. M. Parkinson, *M.Sc.**

SOME years ago one of us made a series of experiments upon the radiation emitted during the explosion and subsequent cooling of inflammable mixtures of coal-gas and air contained in a closed vessel †. Some experiments of a similar kind were also made with hydrogen-air mixtures ‡. In the present paper radiation measurements are recorded with mixtures containing CO, H_2, CO and H_2 in varying proportions, CH_4, C_2H_2, and C_2H_4.

The experiments show that the total radiation emitted during the explosion and subsequent cooling of CO

* Communicated by the Authors.

† Phil. Trans. A, vol. ccxi. p. 375 (1911).

‡ Proc. Roy. Soc. A, vol. xcviii. p. 303 (1920).

mixtures was greater than that emitted by H_2 mixtures of comparable strength, and that in mixtures containing CO and H_2 in varying proportions the total radiation decreased as the hydrogen content increased. In this respect our experiments yield similar results to those obtained by Professor W. E. Garner, but our results are shown to be due to the fact that, owing to their slower explosion and slower cooling, CO mixtures and CO–H_2 mixtures containing large proportions of CO are maintained at radiating temperatures for a longer time than H_2 mixtures and CO–H_2 mixtures containing a large proportion of H_2. Indeed, on analysis of our results we find that the rate of emission from the H_2 mixtures is greater than from the CO mixtures at corresponding temperatures (as inferred from the gas pressures), and it would appear to be entirely due to the time factor that the total radiation from CO mixtures is greater than that from H_2 mixtures.

It was somewhat startling to find that the rate of emission from the H_2 mixtures was greater than that from the CO mixtures at corresponding temperatures, for it is hardly likely that H_2O molecules radiate more powerfully than CO_2 molecules under these conditions. We thought, as a possible explanation, that H_2 mixtures after explosion were more transparent than CO mixtures, but experiments designed to test this showed that there was very little in it. We think that the most probable explanation is in terms of larger temperature differences existing in the H_2 mixtures during cooling after explosion, though experiments in which violent turbulence was arranged with the object of securing uniform temperatures throughout our explosion vessel have failed to substantiate this.

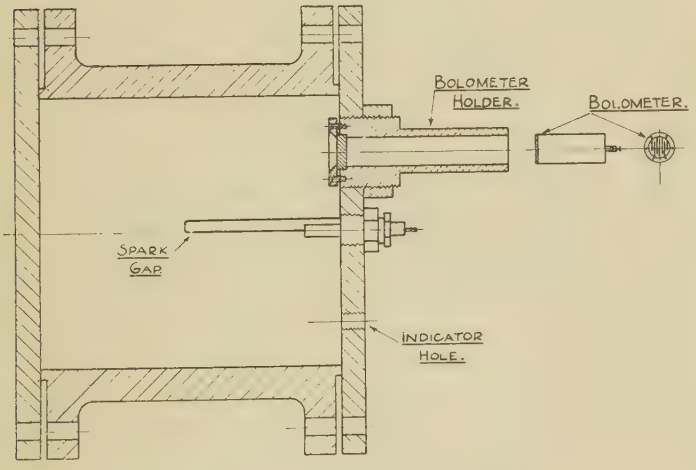
Other experiments in this laboratory suggest that further light may be thrown on this matter by the use of vessels of different sizes, and for this we hope to arrange accordingly. Meanwhile it is of interest to note that from the experiments that we have already made there is no reasonable doubt that the rate of heat loss by radiation from the working fluid in internal combustion engines will be greater the greater the ratio of H_2O/CO_2 in the fluid after combustion at any given temperature when the temperature is inferred from the indicator diagram. This point we have further tested by experi-

ments with hydrocarbon fuels with different hydrogen/carbon contents.

Description of Apparatus.

The explosion vessel used in these experiments consisted of a cast-iron cylinder fitted with flat end-covers. One end-cover carried a Hopkinson optical indicator, multiple filling valve, bolometer holder, and ignition plug. The spark-gap of this plug was at the centre of the explosion vessel. The internal measurements of the vessel were

Fig. 1.



29·2 cm. diameter by 32·4 cm. long. It is shown in fig. 1 in sectional plan.

The bolometer, the surface of which was blackened with camphor smoke, was cut in the form of a circular grid. It was 1 inch in diameter, 0·008 inch thick, and weighed 1·9630 gram. It was mounted on an ebonite plug, which fitted into a brass holder, and which in turn carried at its inner end a fluorite window through which the radiation from the hot gases was transmitted.

The rise of resistance of the bolometer, and therefore its rise of temperature, as radiation from the exploded gases fell upon it after transmission through the fluorite window, was recorded by means of a galvanometer

of the torsion-string type with a natural period of vibration of the order of 0·02 sec.

The electrical circuit was similar to that employed in the early experiments. A large resistance was placed in series with the bolometer, and a small steady current was maintained in the circuit by a battery of secondary cells; the potential difference across the bolometer under these conditions was proportional to its resistance, since any change in the resistance of the bolometer itself had no measurable effect on the current flowing in the circuit.

The galvanometer was connected to the terminals of the bolometer through a small adjustable resistance, across which a small potential difference was maintained to balance the potential difference across the bolometer at room temperature. The deflexion of the galvanometer thus indicated the rise of temperature of the bolometer above that of the room.

The results were corrected for absorption by the fluorite window and for the reflexion from the blackened surface of the bolometer. The piece of fluorite used was found experimentally to transmit 90 per cent. of the radiation falling upon it between very wide wave-length limits. Féry's value of 5 per cent. for the second correction between approximately the same limits was used. Experiments were also made using the bolometer both black and polished to find if the coating of camphor smoke caused any time lag in the radiation record, but none could be detected.

The relationship between the rise in temperature of the bolometer and the deflexion of the galvanometer was found by immersing the bolometer in distilled water in a Dewar flask, and measuring the galvanometer deflexion as the temperature of the water was raised.

Pressure records, from which were deduced mean gas temperatures, were obtained by means of the Hopkinson optical indicator.

The mirrors of the galvanometer and the indicator were made to project spots of light on to a photographic film wrapped round a drum, rotating at a known speed. By this means radiation-time and pressure-time records were obtained simultaneously.

The explosion vessel was filled with the inflammable gases in their correct proportions—as deduced from their

partial pressures—after being evacuated and refilled with air several times in order to clear out all residual gases from the previous explosion. After introducing the inflammable gases air was allowed to rush in up to atmospheric pressure, and to make certain that the mixture was perfectly homogeneous it was allowed to stand for half an hour before being fired by a spark, which was timed by a cam and contact breaker on the film drum. The moment of the passage of the spark was recorded on the film, upon which the pressure and the radiation were recorded.

Result of Experiments.

Carbon-Monoxide, Hydrogen and Air Mixtures.

In the experiments to be described in this section mixtures of CO, H_2, and air in various proportions were exploded at atmospheric temperature and density.

Two series of explosions were made. In each series the total proportion of inflammable gas to air was kept constant, but the proportion of CO and H_2 was varied. In the first series the total proportion of inflammable gas was 30 per cent, and in the other it was 20 per cent. The following table shows the composition of the mixture :—

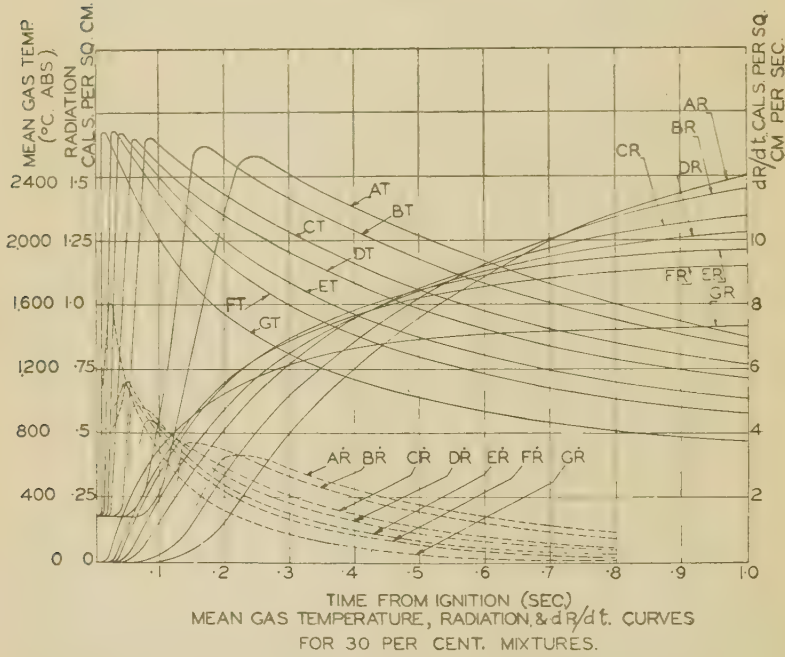
Table I.

	Strong mixture.	Weak mixture.	Ratio $\frac{\%\ CO}{\%\ CO+\%\ H_2}$
A.	30 % CO+air.	—	1·000
B.	29·5 % CO+0·5 % H_2+air.	19·66 % CO+0·34 H_2+air.	0·984
C.	27·5 % CO+2·5 % H_2+air.	18·33 % CO+1·67 % H_2+air.	0·916
D.	25 % CO+5 %+air.	16·66 % CO+3·34 % H_2+air.	0·834
E.	20 % CO+10 % H_2+air.	13·33 % CO+6·67 H_2+air.	0·666
F.	15 % CO+15 % H_2+air.	10 % CO+10 % H_2+air.	0·500
G.	30 % H_2+air.	20 % H_2+air.	0·000

The curves shown in fig. 2 relate to the 30 per cent. mixtures and those in fig. 3 to the 20 per cent. mixtures. Curves AT, BT . . . . etc. are the mean gas temperature curves for these mixtures respectively. These have been calculated from the pressure records by means of the

equation $PV=RT$ after making an allowance for the contraction of volume which takes place on combustion. Curves AR, BR . . . . etc. represent the radiation received by the walls in calories per sq. cm. of surface. Curves $\dot{A}R$, $\dot{B}R$ . . . . etc. are the differentials of the radiation curves, and give the rate at which the walls of the vessel received the radiation in calories per sq. cm. per second.

Fig. 2.



An examination of the curves in figs. 2 and 3 shows that the effect of replacing CO by H_2 is (*a*) to decrease the time of explosion, (*b*) to increase the rate of cooling of the products of combustion, and (*c*) to decrease the total radiation emitted by the products of combustion.

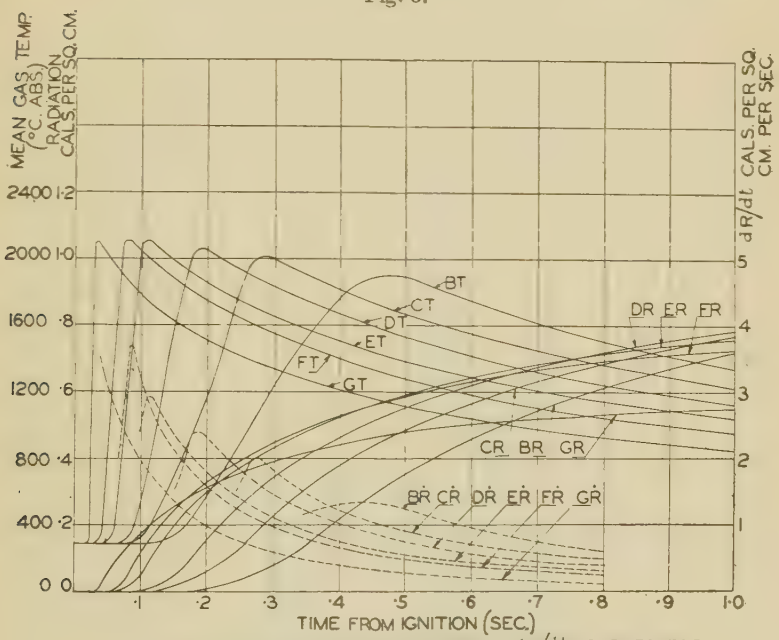
It is interesting to note that the radiation emitted up to the moment of maximum pressure also steadily decreases with the addition of H_2 until, in the case of the rapidly burning 30 per cent. H_2 mixture, no radiation is recorded up to this point. This will be seen from an examination of the figures in Table II. The explanation is clearly

that the time of explosion decreases markedly as the hydrogen content is increased.

The radiation curves in figs. 2 and 3 are not carried sufficiently far to show their maximum values, and Table III. showing these has therefore been prepared.

It will be seen from Table III. that the total radiation emitted during explosion and cooling also decreases as the

Fig. 3.



MEAN GAS TEMPERATURE, RADIATION & dR/dt. CURVES FOR 20 PER CENT. MIXTURES.

hydrogen content is increased. Similar results have been obtained by Garner and Johnson *. These experimenters, working with CO–H_2–O_2 mixtures, employed explosion vessels consisting of metal tubes 1 inch in diameter, and measured the radiation from the exploded gases transmitted through a fluorite plate at the end of the tube. They assumed that, owing to the small bore of the explosion tube, the gases behind the travelling flame front were immediately cooled, and that therefore

* Journ. Chem. Soc. vol. i. p. 281 (1928).

the bulk of the radiation they measured came from the flame front and was of chemical origin.

Luminosity experiments carried out in glass tubes in our laboratory suggest that the cooling of the gases behind the flame front in narrow tubes is not so rapid as might be supposed, and we are of opinion that a great

TABLE II.

Radiation emitted up to the Time of Maximum Pressure.

A. 30 per cent. mixtures.

Mixture.	Time of explosion * (sec.).	Mean gas temp. °C. (abs.).	Radiation.	
			Cals. per sq. cm.	Per cent. heat of combustion (nett).
A	0·240	2530	0·305	6·930
B	·165	2595	·204	4·660
C	·085	2640	·108	2·470
D	·060	2640	·080	1·830
E	·039	2680	·040	0·916
F	·029	2690	·023	0·573
G	·014	2690	·000	0·000

B. 20 per cent. mixtures.

B	0·468	1905	0·310	10·97
C	·282	2020	·197	6·99
D	·189	2065	·137	4·86
E	·107	2115	·078	2·76
F	·080	2120	·044	1·55
G	·033	2110	·005	0·17

* Measured from passage of spark.

deal of radiation measured in this way comes from gases behind the flame front. We therefore incline to the view that the same interpretation will apply both to their result and to ours.

In our experiments it seems clear that the decrease in the total radiation with an increase of the hydrogen content is due to the fact that in virtue of more rapid explosion and also more rapid cooling the time during

which the hot gases are maintained at radiating temperature is decreased. This becomes at once clear from an inspection of the curves in figs. 2 and 3.

An examination of the curves in fig. 4, in which the rate of emission of radiation from the hot gases is plotted against the mean gas temperatures as inferred from the

TABLE III.

Total Radiation emitted during Explosion and subsequent Cooling.

A. 30 per cent. mixtures.

Mixture.	Time from ignition (sec.).	Radiation.	
		Cals. per sq. cm.	Per cent. heat of combustion (nett.)
A	1·70	1·673	38·02
B	1·70	1·616	36·82
C	1·70	1·457	33·30
D	1·60	1·445	33·03
E	1·50	1·258	28·82
F	1·30	1·178	26·98
G	1·10	0·931	21·32

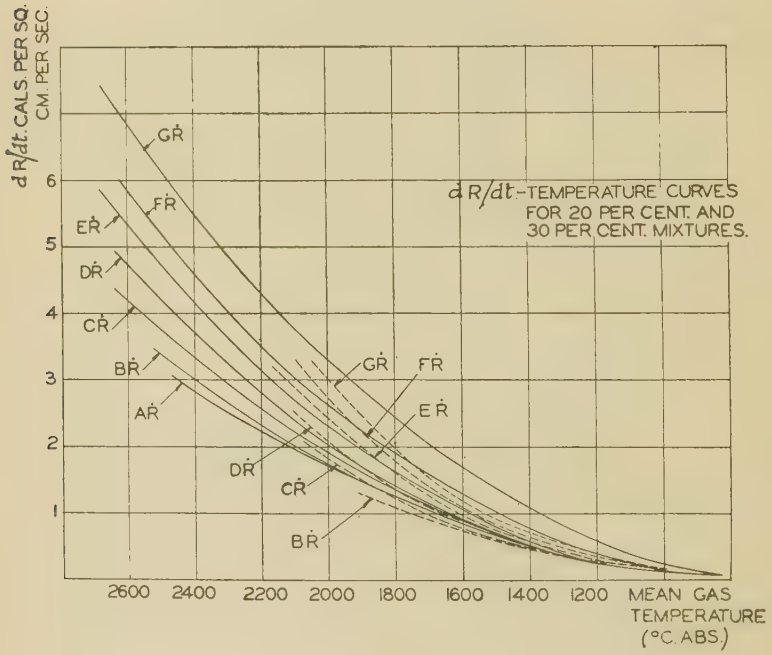
B. 20 per cent. mixtures.

B	2·3	0·904	32·08
C	2·2	·912	32·37
D	1·9	·885	31·35
E	1·8	·843	29·80
F	1·7	·784	27·72
G	1·3	·571	19·74

pressures, shows indeed that the time factor is of overwhelming importance, for it will be seen from them that at any given mean gas temperature, as inferred from the pressure, the rate of radiation from the hot gases is considerably greater the greater the hydrogen content, and that therefore it is only the shorter time during which the gases are at radiating temperatures which causes the total radiation to be decreased with increase of hydrogen content.

The result that the emission of radiation from the gases at any given temperature (as inferred from the pressure) increased as the hydrogen content increased was unexpected. At first sight it would appear that the H_2O molecule radiates more powerfully than the CO_2 molecule; but this view is probably untenable, for the experiments of many investigators seem to show that CO_2 is the more powerful radiator.

Fig. 4.



Two possible explanations will at once occur to the mind, viz.: (1) that H_2O may be more transparent to the radiation it emits than CO_2 to its radiation, and (2) that larger temperature variations may occur in the exploded gases the larger the proportion of H_2O present.

Experiments designed to test whether either of these explanations would cover our results will now be described.

The first set of experiments was designed to measure the transparency of the exploded gases with varying hydrogen content. This was effected by measuring the

radiation from a cone of gas of small solid angle of the length of the explosion vessel and also from a cone virtually nearly twice this length, obtained by polishing a portion of the silver-plated end-cover of the explosion chamber opposite the bolometer. The effective lengths obtained by this means were 32·4 cm. and 63·8 cm. (the reflecting power of the silver-plated end-cover was taken to be 0·97). The values obtained were divided by the solid angle of the cone, to give the radiation from unit solid angle. This is known as the "intrinsic radiance."

TABLE IV.

Mean gas temp. °C. abs.	Ratio $\frac{\text{intrinsic radiance from 63·8 cm.}}{\text{intrinsic radiance from 32·4 cm.}}$		
	29·5 % CO+0·5 % H_2.	15 % CO+15 % H_2.	30 % H_2.
2600	1·23	1·28	—
2500	1·24	1·29	—
2400	1·25	1·29	1·30
2300	1·26	1·29	1·29
2200	1·27	1·29	1·29
2100	1·27	1·30	1·28
2000	1·28	1·29	1·28
1900	1·30	1·29	1·27
1800	1·32	1·29	1·26
1700	1·33	1·29	1·25
1600	1·36	1·28	1·25
1500	1·38	1·25	1·23

The results obtained for the various mixtures used are set out in Table IV. In the table the values of the ratio $\frac{\text{intrinsic radiance from 63·8 cm.}}{\text{intrinsic radiance from 32·4 cm.}}$ at various temperatures during cooling are given for three mixtures with varying hydrogen content.

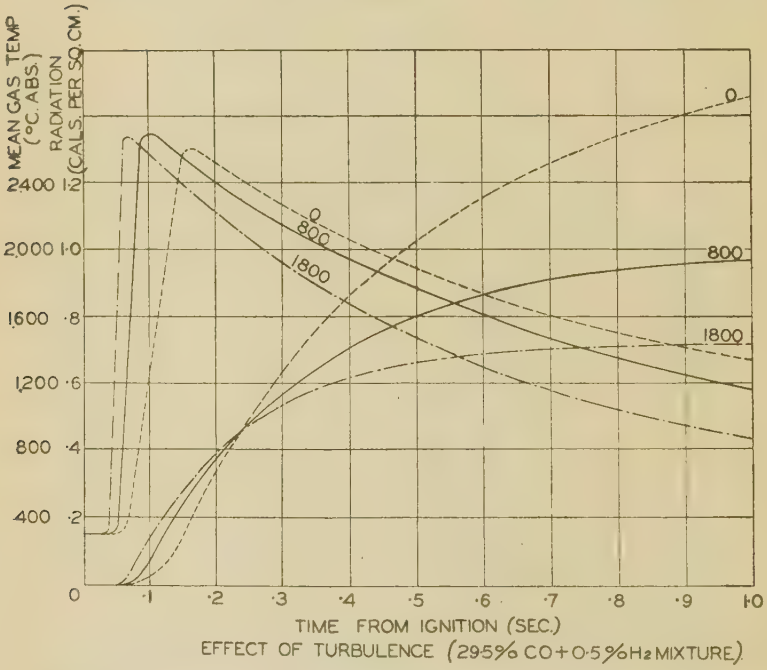
The figures in this table show that the transparency of the mixtures is not widely different, and consequently our results cannot be explained in terms of transparency.

The second suggested explanation, that larger temperature variations may occur in the exploded gases the larger the proportion of H_2O present in the products of combustion, was tested for by attempting to obtain,

by means of violent turbulence, a more uniform distribution of temperature in the exploded gases. The turbulence was obtained by introducing a fan into the explosion vessel and running it at a high speed. The fan was driven by a small electric motor, the speed of which could be varied at will.

The experiments were made with (1) 29·5 per cent.

Fig. 5.



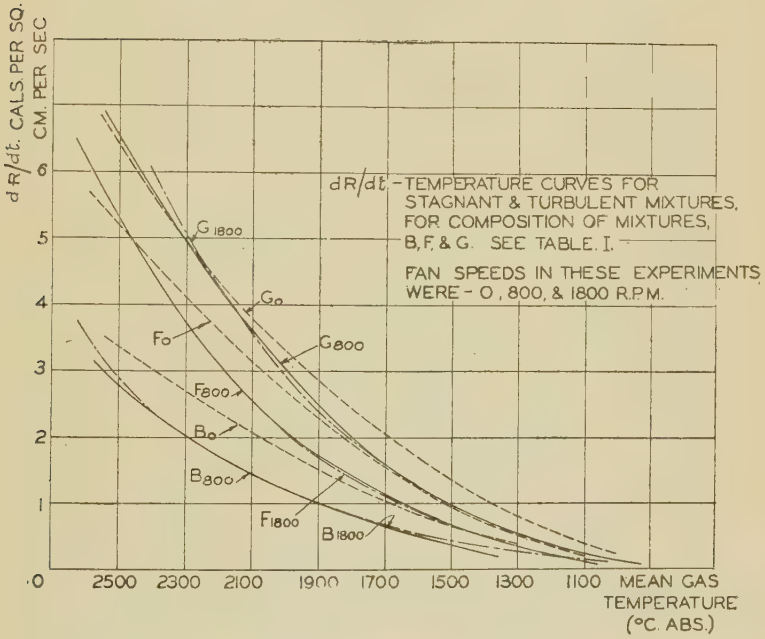
CO+0·5 per cent. H_2 and air, (2) 15 per cent. CO+15 per cent. H_2+air, and (3) 30 per cent. H_2+air mixtures.

The gas temperature curves in fig. 5 show, as would have been expected, that an increase in turbulence causes a decrease in the time of the explosion and an increase in the rapidity of cooling, and consequently a reduction in total radiation. (For the sake of clearness only one set of curves is shown in fig. 5.)

In fig. 6, which shows the rate of emission of radiation $\left(\frac{dR}{dt}\right)$ plotted against a mean gas temperature base,

it is seen that the curves for the two widely different fan speeds shown are practically coincident, but the values of $\frac{dR}{dt}$ are very much lower than in the case when the fan was at rest. This would seem to suggest that while wider temperature differences exist in the stagnant mixtures than in the turbulent mixtures, we have secured

Fig. 6.



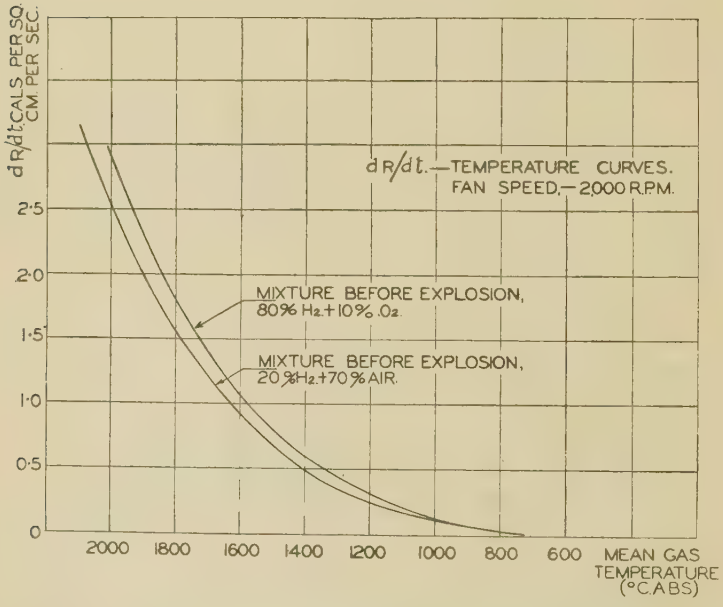
sufficient turbulence to even out temperature differences as far as it is possible to do so.

Confining the attention then to the results for the various mixtures with turbulence, it is at once clear that the $\frac{dR}{dt}$ values for any given mean gas temperature—as inferred from the pressure—increases with the hydrogen content exactly as was found to be the case when experimenting with stagnant mixtures.

With the object of further testing the effectiveness of turbulence in evening out temperature differences, some

experiments were made with mixtures in which diluents of widely different conductivities were employed. Two mixtures were experimented with, each giving 20 per cent. H_2O on combustion, but in the one the diluent was hydrogen and in the other nitrogen—with a little excess oxygen. Turbulence was produced with the fan running at 2000 r.p.m. The results are shown in fig. 7, where $\frac{dR}{dt}$ is plotted against the mean gas temperature. The

Fig. 7.



rate of cooling of the hydrogen diluted mixture was, of course, in virtue of its high conductivity, very much greater than in the nitrogen mixture, though, as will be seen from the curves in this figure, the rates of radiation emitted at any mean gas temperature were not very different in the two mixtures.

In spite of these experiments, however, we incline to the view that temperature differences may explain our results, and we hope that experiments with vessels of different sizes will throw more light on the matter.

Methane, Acetylene, Ethylene and Air Mixtures.

Experiments were next carried out with mixtures of hydrocarbons and air. Three hydrocarbon gases were used, viz., methane, acetylene, and ethylene; and assuming complete combustion, the ratio of CO_2 to H_2O in the products of combustion of these gases was 1 : 2, 2 : 1, and 1 : 1 respectively.

A series of experiments was made with each of the three gases. All the explosions were made with the fan inside the vessel running at 2000 r.p.m.

The experiments showed that the rate of emission of radiation (dR/dt) at any given temperature (as inferred from the pressure) during the cooling period was precisely the same as that given under similar conditions of turbulence and density by the mixtures of CO and H_2.

Origin of the Radiation.

The experiments described in this paper confirm the earlier experiments made by one of us in showing that the bulk of the total radiation from the exploded gases is emitted during the cooling period, and that therefore it is mainly of thermal origin. The amount of radiation emitted during the explosion is always—unless the time of explosion is exceptionally large—a small proportion of the total, but even this small amount seems to be governed primarily by the time of the explosion and the temperature attained. That this is so will at once become obvious from an inspection of the figures in Table II.; indeed, it will be seen that in an extremely rapid explosion, such as the 30 per cent. hydrogen-air mixture produces, no radiation is measurable by our apparatus up to the point of maximum pressure.

It might be thought that this is possibly due to the black coating on the bolometer producing an insulating and lagging effect; it has been shown, however, that this is not the case, for on repeating the experiments with the platinum bolometer polished, thus relying upon the natural absorption power of platinum, and greatly increasing the sensitivity of the recording, the result was the same *. We are satisfied after many experiments

* It is a curious result that on examination of our records under powerful magnification radiation from similar explosions began to be recorded by means of the blackened bolometer *before* that recorded by means of the polished bolometer. The difference was exceedingly small, and we do not care to affirm definitely, but as a result of several experiments we think the fact is as stated.

that the radiation emitted during the explosion period in this particular mixture could not possibly have exceeded one-tenth of one per cent. of its heat of combustion, and was probably a good deal less than this figure. In view of the fact that the vast bulk of the chemical activity takes place during the explosion period, it would not therefore seem that much of the radiation emitted by the exploded gases is of chemical origin.

Against this is the fact brought to light by the earlier experiments with coal-gas mixtures *, and confirmed by our present experiments with CO mixtures, that the rate of emission of radiation from the exploding gases is in certain cases rather greater at some moment during the explosion period than at the moment of maximum pressure (see dotted curves in figs. 2 and 3). This result had previously been interpreted as showing that a certain amount of radiation emitted during the explosion period was of chemical origin †. While we think that this view should not be definitely ruled out, we feel that in the light of our present experiments there is a possibility that the result may be explained in terms of temperature.

We are led to suggest this because it is in slow-burning mixtures that this result is particularly noticeable. In such mixtures there may be time for convection to raise the hot core which is in process of formation during the explosion period to a position in which, by the time maximum pressure is reached it has become marginal as regards the radiation field influencing the bolometer. This is a matter to be settled by further experiment. Meanwhile it seems safe to assume that chemical radiation, even if at all appreciable, is but a small proportion of the total.

In putting forward this view our suggestion is not that there is no chemiluminescence, but that the energy in it, as measured by a bolometer, is very small—perhaps negligibly so—in comparison with that of the thermal radiation.

We wish to thank the Department of Scientific and Industrial Research for a maintenance grant for one of us (R. M. P.), without which it would not have been possible to carry out these experiments.

* Phil. Trans. A, vol. ccxi. p. 375 (1911).
† Phil. Trans. A, vol. ccxi. p. 325 (1911).

XIX. *Note on Raman Effect.* *By* A. Ganguli*.

In a previous paper (Phil. Mag. xiii. p. 306 (1931)) the Raman effect was considered from the aspect of unimolecular reactions, and the intensity ratios between the Stokes and anti-Stokes lines were deduced for the two cases when $h\nu << kT$ and $h\nu >> kT$. Since then Prof. Raman has kindly pointed out to the writer that the formula for the case $h\nu >> kT$ is not in agreement with the experimental results. In the present note the method of the last paper is revised and the results are modified.

Before proceeding, some mistakes of the previous paper are corrected as follows :—

In equation (1) *read* $\left(\frac{\nu-\nu_i}{\nu+\nu}\right)^4$ *instead of* $\left(\frac{\nu-\nu}{\nu+\nu}\right)^4$.

In equation (7) *read* $\frac{1}{1-e^{-h\nu'/kT}}$ *instead of* $\frac{1}{1-e^{h\nu'/kT}}$.

Page 306, line 6 from the bottom, *read* p. 360 *instead of* p. 363.

Page 306, line 5 from the bottom, *read* lxviii. *instead of* lxiii.

In calculating the number of molecules passing into the nth and mth from the activated states a_1 and a_2 respectively, it was assumed after Christiansen (*Zeits. Phys. Chem.* ciii. p. 91 (1922)) that the probabilities of spontaneous emission ($A^n_{a_1}$ and $A^n_{a_2}$) were equal to the frequencies ν' and ν'' of the radiations emitted in the two cases. The recent development of the new quantum mechanics indicates, however, that the A-coefficient $= k\nu^3 |P_{rs}|^2$, where ν is the frequency of the emitted radiation, P_{rs} is the electric moment vector, and k is a constant (Kramers and Heisenberg, *Zeit. f. Phys.* xxxi. p. 681 (1925) ; Dirac, Proc. Roy. Soc. cxii. p. 661 (1926)). Assuming that P_{rs} is constant in all the processes, equations (8) and (9) and also (11) and (12) of the previous paper are to be modified. Thus we have, for the number of molecules passing from the state $a_1 \longrightarrow n$,

$$\frac{dN_{a_1}}{dt} = c \cdot N_m \cdot e^{-\frac{h\nu}{kT}} \cdot \nu'^2 \frac{kT}{h} \qquad (h\nu' << kT) \quad . \quad (1\,a)$$

$$= c \cdot N_m \cdot e^{-\frac{h\nu}{kT}} \nu'^3 \qquad (h\nu >> kT). \quad (1\,b)$$

* Communicated by Prof. K. C. Kar, D.Sc.

Hence the number of molecules passing from the state $m \longrightarrow n$ per unit time,

$$\frac{dN_m}{dt} = N_{mn} = \frac{dN_{a_1}}{dt} \cdot e^{\frac{h\nu}{kT}} \qquad \left[\because N_{a_1} = N_m e^{-\frac{h\nu}{kT}}\right]$$

$$= c \cdot N_m \cdot \nu'^2 \cdot \frac{kT}{h} \qquad (h\nu' << kT) \quad . \quad (2\,a)$$

$$= c \cdot N_m \cdot \nu'^3 \qquad (h\nu' >> kT). \quad . \quad (2\,b)$$

If the molecule is considered to be an oscillator giving out energy $h\nu'$,

$$E_S = N_{mn} \cdot h\nu' = c \cdot N_m \nu'^3 \cdot kT \qquad (h\nu' << kT), \quad (3\,a)$$

$$E_S = c \cdot N_m \cdot h\nu'^4 \qquad (h\nu' >> kT). \quad (3\,b)$$

Similarly for the anti-Stokes radiation we have, instead of (11 *a*) and (11 *b*) of the previous paper,

$$\frac{dN_{a_2}}{dt} = c \cdot N_m \cdot e^{-\frac{h(\nu-\nu')}{kT}} \cdot \nu'^2 \frac{kT}{h} e^{-\frac{h\nu}{kT}} \qquad (h\nu'' << kT) \quad (4\,a)$$

$$= c \cdot N_m e^{-\frac{h(\nu-\nu')}{kT}} \cdot e^{-\frac{h\nu}{kT}} \cdot \nu''^3 \qquad (h\nu'' >> kT). \quad (4\,b)$$

Hence

$$\frac{dN_n'}{dt} = N_{nm} = cN_m e^{-\frac{h(\nu-\nu')}{kT}} \nu''^2 \frac{kT}{h} \qquad (h\nu'' << kT) \quad . \quad (5\,a)$$

$$= c \cdot N_m \cdot e^{-\frac{h(\nu-\nu')}{kT}} \cdot \nu'^3 \qquad (h\nu'' >> kT) \quad . \quad (5\,b)$$

and

$$E_{AS} = N_{nm} h\nu'' = c \cdot N_m e^{-\frac{h\nu_i}{kT}} \cdot \nu'^3 kT \qquad (h\nu << kT) \quad (6\,a)$$

$$E_{SA} = c \cdot N_m \cdot e^{-\frac{h\nu_i}{kT}} \cdot h\nu'^4 \qquad (h\nu >> kT). \quad (6\,b)$$

Thus

$$\frac{I_S}{I_{AS}} = \frac{E_S}{E_{AS}} = \frac{\nu'^2}{\nu''^2} \cdot e^{\frac{h\nu_i}{kT}} = \left(\frac{\nu-\nu_i}{\nu+\nu_i}\right)^3 e^{\frac{h\nu_i}{kT}} \qquad (h\nu << kT), \quad (7\,a)$$

$$\frac{I_S}{I_{AS}} = \frac{\nu'^4}{\nu''^4} \cdot e^{\frac{h\nu_i}{kT}} = \left(\frac{\nu-\nu_i}{\nu+\nu_i}\right)^4 e^{\frac{h\nu_i}{kT}} \qquad (h\nu >> kT). \quad (7\,b)$$

We thus obtain the third and the fourth power laws for the two cases. It may be noted that under experimental conditions $h\nu >> kT$, and hence equation (7 *b*) is valid. This formula has been verified by Sircar (Ind. J. Phys. v. p. 159; vi. p. 131) and Bhagvantam (*ibid.* vii. p. 106). For the

intensities of Stokes lines of different frequencies it follows from equation (3 *b*),

$$\frac{I_{S_1}}{I_{S_2}} = \left(\frac{\nu_1 - \nu_i}{\nu_2 - \nu_i}\right)^4 . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

With the modified forms of the equations for the numbers N_{mn}, N_{nm}, the equations (14 *a*) and (14 *b*) of the previous paper are transformed as follows:

$$\frac{I_S}{I_{AS}} = \frac{N_{mn}}{N_{nm}} = \left(\frac{\nu - \nu_i}{\nu + \nu_i}\right)^2 e^{\frac{h\nu_i}{kT}} \qquad (h\nu << kT), \quad . \quad (9\,a)$$

$$\frac{I_S}{I_{SA}} = \frac{N_{mn}}{N_{nm}} = \left(\frac{\nu - \nu}{\nu + \nu_i}\right)^3 e^{\frac{h\nu_i}{kT}} \qquad (h\nu >> kT), \quad . \quad (9\,b)$$

which give the intensity ratios, according to Raman, as the ratio of the numbers of molecules passing to the nth and mth states.

It may be pointed out that the experimental results can be explained by the third power as well, and it is difficult to choose between formulæ (7 *b*) and (9 *b*).

Recently Placzek (*Zeit. f. Phys.* lviii. p. 583 (1931)) has also obtained the fourth power law by following the method of Einstein and Ehrenfest (*Zeit. f. Phys.* xix. p. 301 (1923)). The following procedure, which is similar to that of Placzek, leads to the foregoing results in a much simpler manner. According to Einstein and Ehrenfest the number of molecules from the state $m \rightarrow n$, by the absorption of $h\nu$ and subsequent emission of $h\nu'$,

$$N_{mn} = n\rho(\nu)b(a_1 + b_2\rho(\nu'))d\nu\, d\Omega\, dt, \quad . \quad . \quad (10)$$

and the number passing from $n \longrightarrow m$,

$$N_{nm} = n'\rho(\nu)b(a_2 + b_2\rho(\nu''))d\nu\, .\, d\Omega\, db\,; \quad . \quad (11)$$

a, b, a_1, b_1, a_2, b_2 are connected in the following manner:—

$$\left.\begin{aligned} &\frac{a}{b} = \frac{8\pi h\nu^3}{c^3}, \quad \frac{a_1}{b_1} = \frac{8\pi h\nu'^3}{c^3}, \quad \frac{a_2}{b_2} = \frac{8\pi h\nu''^3}{c^3} \\ \text{and} \quad &n' = n\,.\,e^{-\frac{h\nu_i}{kT}}. \end{aligned}\right\} \quad (12)$$

Again taking a, a_1, a_2, proportional to ν^3, ν'^3, ν''^3 respectively,

$$\frac{I_S}{I_{AS}} = \frac{N_{mn}\,.\,h\nu'}{N_{nm}h\nu''} = \frac{(a_1 + b_1\rho(\nu'))\nu'}{(a_2 + b_2\rho(\nu''))\nu''} e^{\frac{h\nu_i}{kT}}$$

$$= \frac{\nu'^4}{\nu''^4} \cdot \left(\frac{1 - e^{-\frac{h\nu''}{kT}}}{1 - e^{-\frac{h\nu'}{kT}}}\right) e^{\frac{h\nu_i}{kT}} . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Or we have again equations (7 *a*) and (7 *b*) for the two cases $h\nu << kT$, $h\nu >> kT$.

Another very simple method of deduction of equations (7 *a*) and (7 *b*) is based on the theory that the life of an activated molecule is inversely proportional to "*a*" (*cf.* Tolman, Statistical Mechanics). Hence the number of molecules passing from $a_1 \longrightarrow n$ is

$$N_{a_1} \cdot a_1 = N_m e^{-\frac{h\nu}{kT}} \cdot a_1.$$

Again, the number of molecules passing from $a_2 \longrightarrow m$ is

$$N_{a_2} \cdot a_2 = N_n' e^{-\frac{h\nu}{kT}} \cdot a_2 = N_m e^{-\frac{h\nu}{kT}} \cdot e^{-\frac{h\nu_i}{kT}} \cdot a_2.$$

From these the intensity relations follow readily.

It is to be noted that the assumption made before, that the electric moment factor is constant, may not strictly be true, since this will be proportional to the frequency of the emitted radiation and the characteristic absorption frequency of the molecule. This leads to a correction term containing the absorption frequency as suggested by Placzek.

Chemical Laboratory,
College Dupleix,
Chandernagere.
April 1932.

XX. *Notices respecting New Books.*

Biographical Fragments. By Sir Arthur Schuster, F.R.S. [Pp. xi+268; with portraits of the author and travel pictures.] (London: MacMillan & Co. Price 10*s.* 6*d.* net.)

NO one has been more closely connected with the development of Physics than the author of these biographical fragments. This remark applies to his own important contributions to science and to his exercise of professorial functions at Owens College, Manchester, to his Secretaryship of the Royal Society, and to his close associateship with the conduct of the British Association for the Advancement of Science and of the important committees connected with it.

It is not, however, with the scientific aspects of his work that this volume deals. It is written with the chief object of preserving some impressions of times and places in which his friends have expressed an interest, and of the personality of some scientific men of a past generation. It does not

claim to be an autobiography, and yet many persons will be mainly interested in the autobiographical details which appear. This applies specially to his early recollections, the Frankfurt Gymnasium, his tutors, how he became a Doctor of Philosophy (at Heidelberg), how he was selected by Norman Lockyer for the Siamese Eclipse Expedition of 1875, and afterwards wandered from Simla through Kulu to Kashmir. All this is told, not for the scientific specialist, but for those who are interested in the human side of things and events.

In the second part (entitled Episodes) an even lighter aspect of things is emphasized. This will be found to be very amusing, though it is doubtful whether it falls within the scope of the 'Philosophical Magazine.' The closest approach is in its last chapter—"How I tried to pull the leg of the British Association at Southport." The paper (with which its leg was to be pulled) does not appear in the official report of the meeting, but it is printed here.

Many will find their greatest interest in the Biographic Byeways with which the volume concludes. These include reminiscences of Leverrier, Joule, Balfour Stewart, Kirchhoff, Boltzmann, Langley, Osborne Reynolds, Stokes, Helmholtz, Hertz, Röntgen, and a very generous tribute to Henry Wilde. To many younger physicists some of these may be merely names: these reminiscences will help to bring them to life.

Report on Band-Spectra of Diatomic Molecules. By W. Jevons, D.Sc. [Pp. 308.] (Published by the Physical Society, 1 Lowther Gardens, London, S.W. 7. Printed by the University Press, Cambridge, 1932. Price 17*s.* 6*d.* net; in cloth, 20*s.* 6*d.*)

Those persons who are vaguely troubled by the immense amount of speculative theory which is at present abounding will be reassured by the evidence afforded in this Report of the correspondingly large amount of experimental work which accompanies it. Even this evidence is limited to what is now known concerning diatomic molecules, the spectra of polyatomic molecules being excluded. Stress is laid upon the observational side of the subject rather than the purely theoretical; the theoretical results given are limited to those necessary for the interpretation of the analyses of bands and band systems. "Some parts of the subject, such as treat of dissociation, isotopy, Raman spectra, which border upon other fields of knowledge, are dealt with at some length"; the subject of valency is, however, not included, being considered to lead too far from the main theme.

The volume is well illustrated by plates and diagrams.

It is a Report which has been badly wanted. It requires great labour for the individual experimentalist to find out what is at present known by consulting the multifarious periodicals, all over the world, in which the work may be described. This labour will now be saved so far as he is concerned ; but it is only saved by the great labour which Jevons must have expended in collecting the material for this Report: it is a fine monument to his labours. The Physical Society has obviously done well in selecting him to carry out the enterprise.

It may be added that "the Report is mainly addressed to the physicist who has not hitherto taken up band-spectra as a subject for special reading or laboratory work." This declaration of the author must not deter the specialist from consulting the volume ; for him it is equally well adapted.

The Cambridge University Press have carried out the printing side in their usual excellent way.

L'Atomistique moderne et la Chimie. Par M. Haissinsky. [Pp. 386, with 47 figs.] (Paris : G. Doin et Cie, 1932. Price 110 francs.)

The Italian original of this book appeared in 1930, but, at the request of Professor Langevin, the author has now prepared a French translation which forms one of the series of publications known as the Collection Langevin-Perrin-Urbain.

The subject-matter covers a very extensive field in that the principal advances which have been made in physical science during the present century fall within its purview. This period is associated with profound changes in the basic interpretation of the experimental facts of physics and chemistry, and the book is of special interest to physical chemists. The various matters discussed include electrons, atoms, molecules, radiations, quanta, atomic and molecular structure, valency, the laws of thermodynamics, energy relations with particular reference to Born's theory, photochemistry, magneto-chemistry, chemical kinetics, catalysis, adsorption, and wave mechanics.

The method of exposition and general style is very attractive, and the treatment gives the impression that the author has a very clear grasp of the significance of the advances which have been made in the various domains of experimental research.

Having regard to the scope of the subject-matter and the size of the present volume, the reader will not expect to find that any of the twenty chapters represents more than a general outline. In its particular sphere it is, however, definitely of outstanding merit, and if the different chapters are not

of equal value this may be largely attributed to the inevitable lack of intimate acquaintance with each individual section of a wide range of subjects.

To students of physics and chemistry who desire to have a thoroughly readable account of recent progress, the book can be confidently recommended.

Il Polarografo, sua teoria e applicazioni. By GIOVANNI SEMERANO. [Pp. iv+207, with 31 figs.] (Padova : Libreria Editrice A. Draghi, 1932. Price 16 lire.)

THIS monograph gives a complete account of the hitherto published work on current-voltage relations, which are disclosed by the use of the dropping mercury cathode. The development of this method for the investigation of cathodic processes, of ionic equilibria in solutions, and of analytical problems is almost entirely the result of research conducted by J. Heyrovsky, Professor of Physical Chemistry in the University of Prague, and a number of collaborators.

The polarograph is an instrument by means of which current-voltage curves are automatically recorded. In the first section the author describes the general theory of these curves and the results which have been obtained in the study of over-voltage, complex ion discharge, and electro-adsorption, and also in the estimation of both inorganic and organic substances. It has been found that the sensitivity of the polarograph in certain analytical processes is extraordinarily high.

The second part deals with the application of the polarograph to physiological, bio-chemical, and industrial problems.

Dr. Semerano's treatment of the subject is to be highly commended for its clearness of exposition and the systematic arrangement of the material. The detailed information relative to the technique of the experimental procedure should be found extremely useful. The monograph affords a complete bibliography of a method of measurement which can be said to have assured its position by the results which it has already produced.

Les Colloides et l'état colloidal. Par A. BOUTARIC. [Pp. 259, 28 figures.] (Libraire Félix Alcan. 18 francs.)

M. BOUTARIC, as a Professor in the Faculty of Science in Dijon, presents this little book as an outline of the course of lectures given by him to students in his University.

An historical introduction is followed by a chapter containing a number of practical hints of value to the student. The remaining

chapters deal in particular with those parts of the subject which have shown themselves amenable to theoretical treatment, although complete exclusion of other topics has not been attempted.

The topics dealt with are those familiar under the headings osmosis, dialysis, brownian movement, electrophoresis, floculation, emulsions, micelles, gels, &c.

The treatment is such as to commend the book in particular to University students.

Electrical Phenomena in Gases. By K. K. Darrow. [Pp. 492, 91 figs.] (Baillière, Tindall, & Cox. Price £2 2*s*.)

Dr. Darrow, associated as he is, so closely with the research activities of the Bell Telephone Laboratories in New York, is singularly well fitted to produce a book of this content and character.

The author, in his preface, takes pains to explain the reason for his choice of title as alternative to that coined by Sir J. J. Thomson many years ago—"Conduction of Electricity through Gases," for what seems to be the same field. His explanations serve the useful purpose of stressing the different directions in which enquiries have been tending in recent years.

The first division, about one-third of the book, presents four chapters dealing broadly with gaseous ionization, excitation, and electron scattering. These phenomena are taken as examples of individual encounters of atomic particles under specified conditions of experiment, and no important work up to quite recent times seems to have been overlooked.

The next five chapters form roughly a quarter of the book and deal in some detail with ions and atoms moving in high density through gases. Here such matters as mobility, diffusion, and recombination receive attention.

The remainder of the book deals, in a sufficiently comprehensive way, with the various space charge and "plasma" effects—including the self-sustaining glow and the arc.

This is a most useful presentation of our knowledge in this field and should be a valuable addition on the book shelves, not only of University students, but of beginners in this interesting field of investigation. Diagrams are clear and numerous, references are well done, and the name and reference indexes are very helpful.

The reviewer particularly likes the matt surface of the paper on which the book is printed, as it makes for specially easy reading.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

FIG. 1.

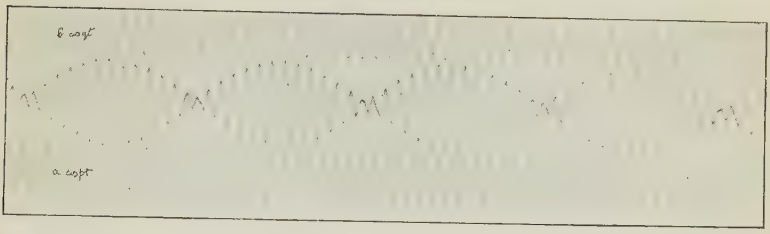


FIG. 2.

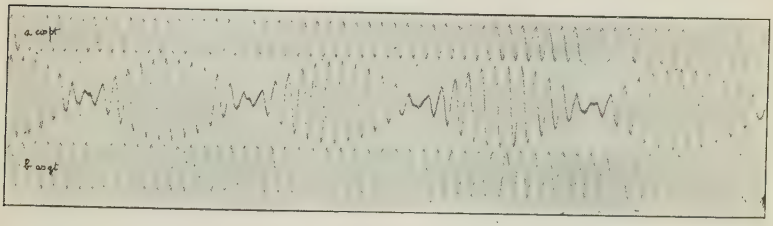


FIG. 3.

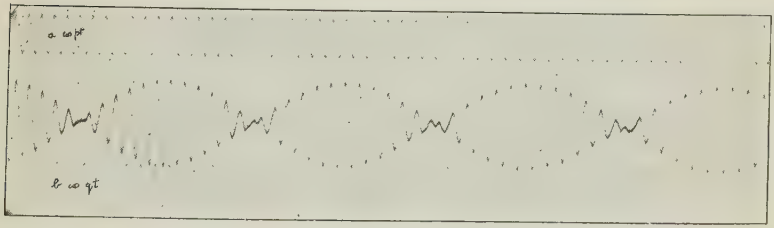


FIG. 4.

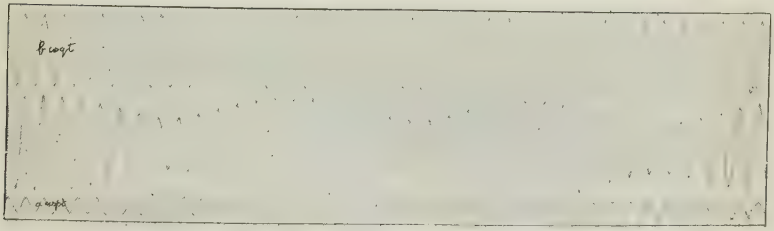


FIG. 5.

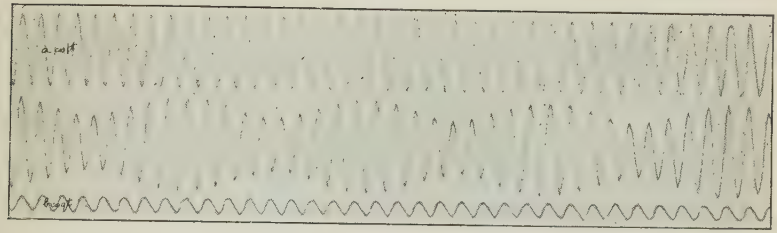


FIG. 6.

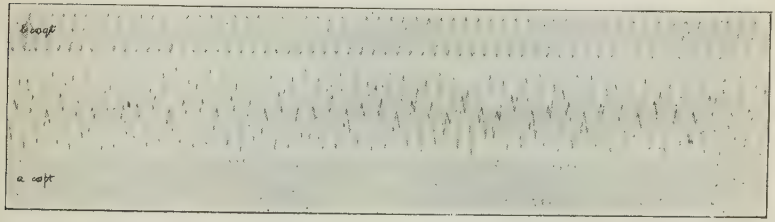


FIG. 7.

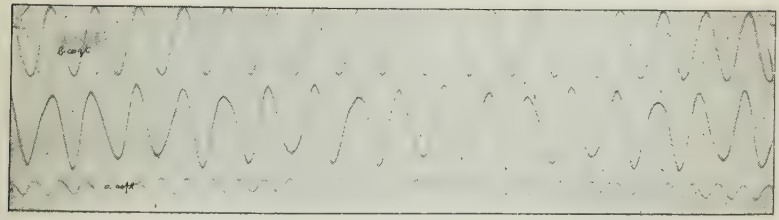


FIG. 8.

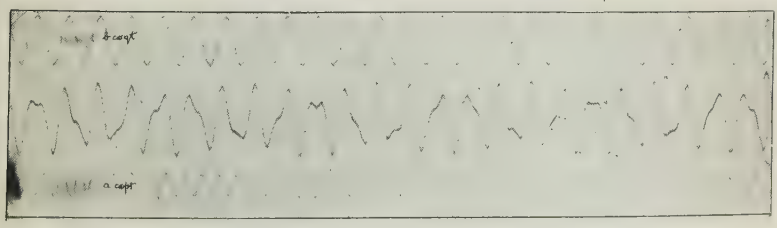


Fig. 1.

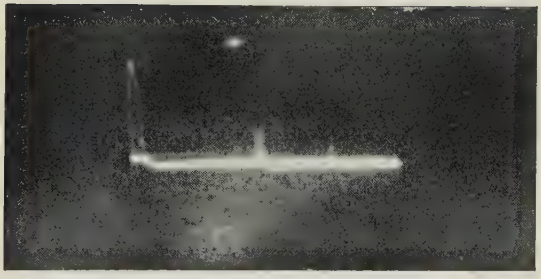


Fig. 2.

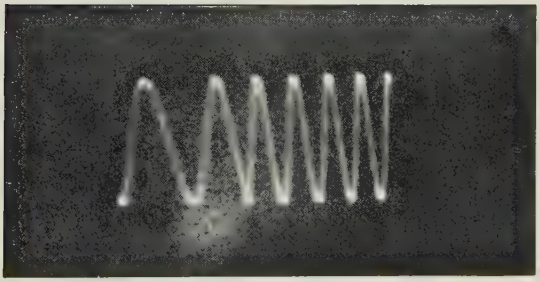
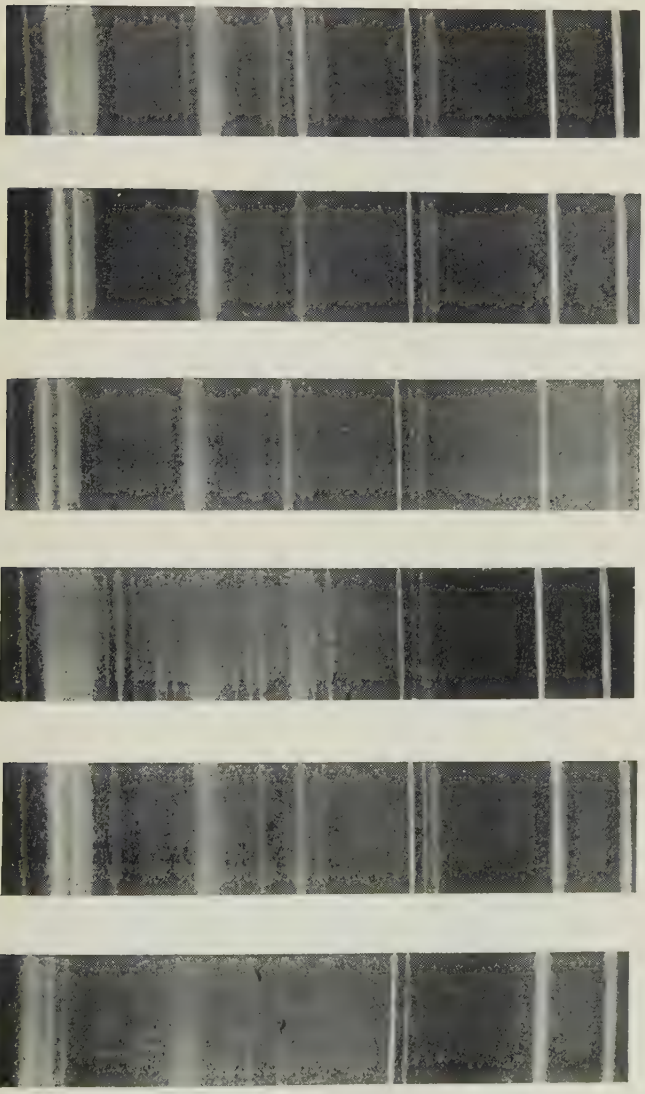


Fig. 1. Oscillographic records of the echoes. Ground signal on the extreme left and the two echoes F_1, F_2 on the right.

Fig. 2. Calibration curve for the time base. Each step is equal to 1/1400 sec.



(*a*) ethyl sulphide.
(*b*) propyl sulphide.
(*c*) iso-butyl sulphide.
(*d*) allyl sulphide.
(*e*) iso-amyl hydrosulphide.
(*f*) thio-glycollic acid.

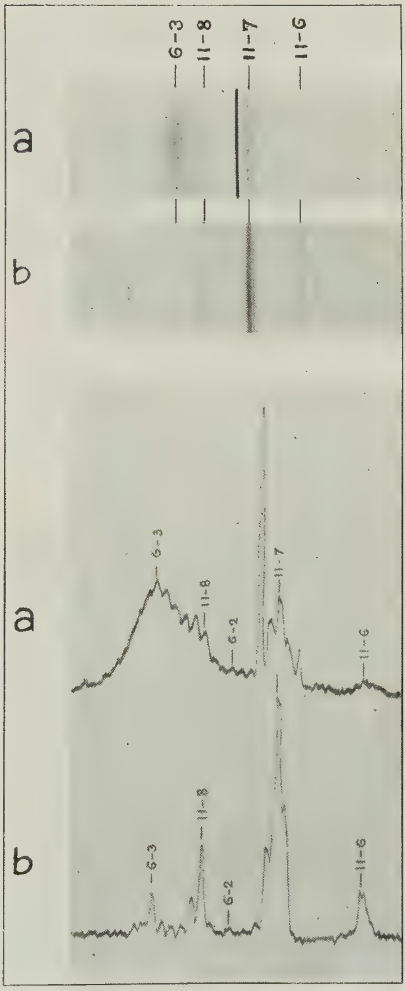

6-3
11-8
11-7
11-6
a
b
a
b
6-3
11-8
6-2
11-7
11-6
6-3
11-8
6-2
11-6

Fig. 1.

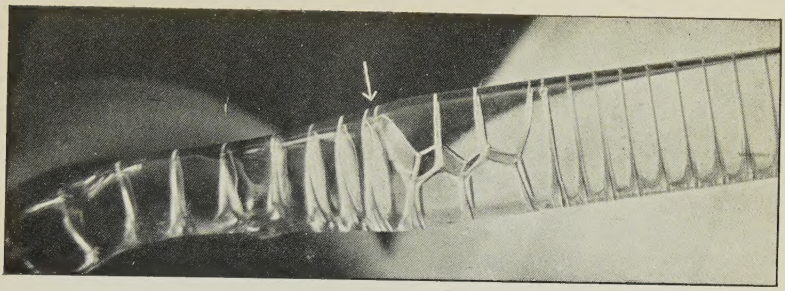


Fig. 2.

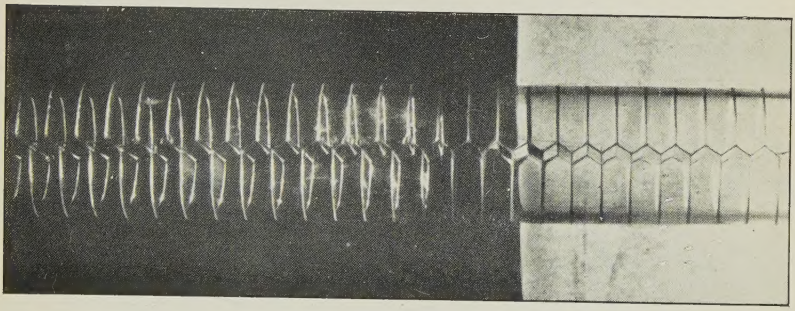


Fig. 3.

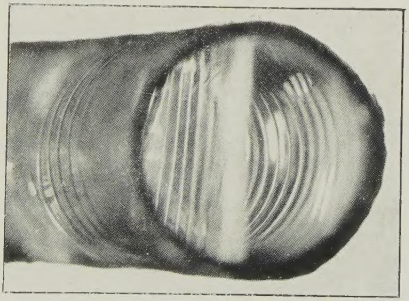


Fig. 4.

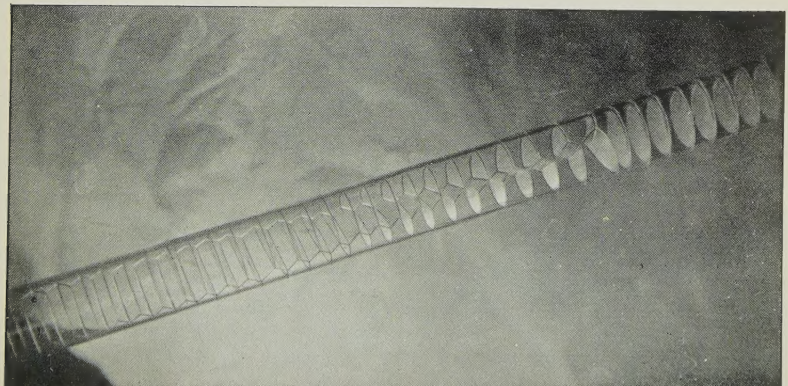


Fig. 5.

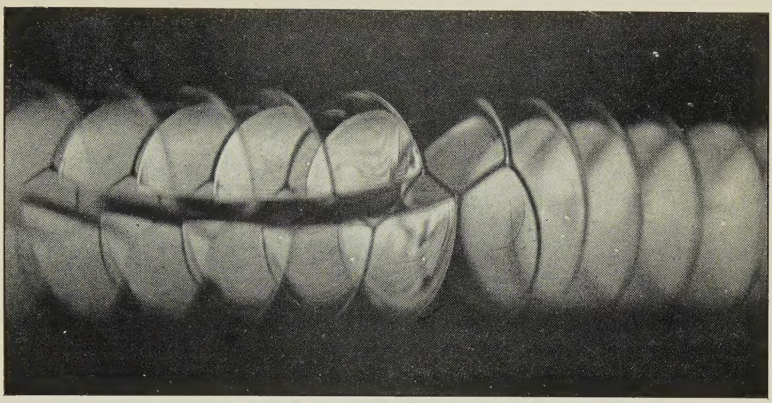


Fig. 6.

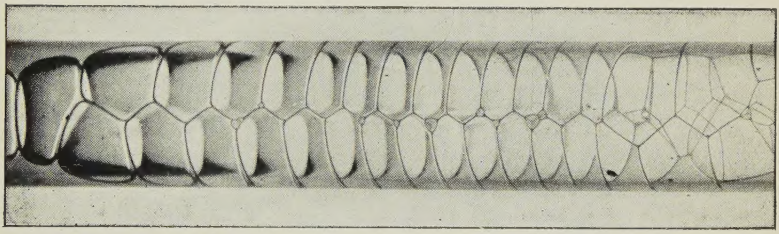


Fig. 7.

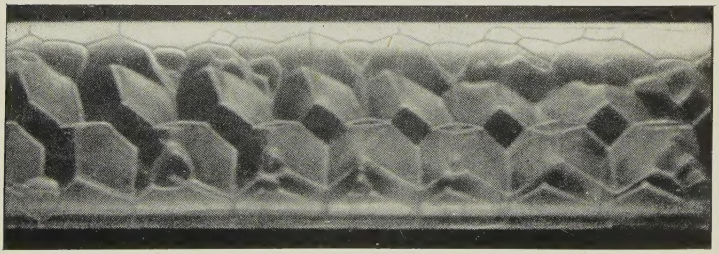


Fig. 8.